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PROCEEDINGS of the CONFERENCE ON NAVAL STORES PRODUCTS

(Adhesives, Tackifiers, and Related Materials)

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FOREWORD

This Conference was sponsored by USDA's Southern Utilization Research and Development Division and the Battelle Memorial Institute. The principal purpose of the Conference was to report research conducted by the Division at its Naval Stores Laboratory in Olustee, Florida, and at the laboratories of Battelle in Columbus, Ohio. An exchange of information was provided for the benefit of future research.

These proceedings report the statements presented by the various speakers during the conference and give an account of the discussions following.

C. H. FISHER, Director
Southern Utilization Research and Development Division

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WELCOME

by

G. E. Goheen
Southern Utilization Research and Development Division

On behalf of the Southern Utilization Research and Development Division (SURDD), it is my pleasure to welcome you to New Orleans. Dr. Fisher, the Director of our Division, regrets that he cannot be present and asked that his greetings be passed on to you. We are glad that you have taken time to visit us and that we have the opportunity of discussing some of our work with you. We trust that it will be of interest and value to you.

For the benefit of those who have limited information about SURDD and the Agricultural Research Service (ARS) of USDA, I would like to explain that the "Southern Regional Research Laboratory" is the designation of our facility here in New Orleans. SURDD headquarters for its nine laboratories are at this location. The Naval Stores Laboratory is one of these and is located at Olustee, Fla., near Jacksonville. Ray V. Lawrence is Chief of this laboratory.

Since you will be hearing about our work on naval stores today, I would like to take a minute to talk about some of our other work. One well-known commercialized development that has resulted from utilization research is the frozen orange juice concentrate. This development worked out by SURDD in cooperation with the Florida Citrus Commission has developed an orange crop into a major new industry amounting to close to $300 million per year. Just the new taxes resulting to the Government for this operation has more than paid for our utilization research.

Other developments include instant sweetpotato flakes, low oil content peanuts, fruit juice mixtures, improved cottonseed meals and flour, high protein rice flour, and new or improved products from cotton such as improved all cotton durable press products, stretch cotton yarn fabrics and garments, flame and rot resistant cotton products, and related items.

SURDD holds several open conferences each year to disseminate information promptly about research accomplished. In addition, research scientists of the Division present papers describing advances in research at various scientific meetings. The research is described also in papers published in various technical journals or in ARS communications. Examples of the latter are the "Evaluation of the Selected Naval Stores Derivatives as Agricultural Chemicals," ARS 72-68, dated January 1969. A semiannual list of Publications and Patents gives brief abstracts of papers published recently by members of the Division. Single copies of reprints may be obtained free by addressing the Division headquarters in New Orleans.

As stated in the foreword to the program for today's meeting, this Conference is sponsored as a cooperative activity by SURDD and the Battelle Memorial Institute. I wish to thank those named on the program who have cooperated in the planning of this Conference and those taking part in it. Dr. Wojcik is SURDD's Assistant Director for Industrial Developments. He will be glad to answer any questions about our products.

We issue a standing and cordial invitation to you to visit us and our scientists, either as a group or individually, at any time to discuss subjects of further interest to you. We hope your stay in New Orleans is a pleasant one.

[J. L. Gillis, Jr., General Chairman, responded to Dr. Goheen's welcoming remarks and commented on the Naval Stores Industry in general.

Mr. Gillis then introduced R. V. Lawrence, Chief of the Naval Stores Laboratory at Olustee, Fla., who presented a resumé of the research being done on the chemistry of pine gum products, including a glimpse of studies on the neutral portion of the rosin.]

SESSION I: D. E. Campbell, Pulp Chemicals Association, New York, N.Y., Chairman

PREPARATION OF NEW NAVAL STORES DERIVATIVES FOR ADHESIVES

by

W. H. Schuller
Naval Stores Laboratory
Olustee, Fla.

The Naval Stores Laboratory in Olustee, Fla., as most of you know, is a field station of the Southern Regional Research Laboratory here in New Orleans. Our goal is to expand the utilization of naval stores. In the course of this work, we have prepared many hundreds of new compounds. The question then arises: "What are these compounds good for?"

In our quest for uses for these new materials, we naturally considered the field of adhesives. This is a traditional area of rosin consumption. The use of rosin in this area is predicted to increase. Therefore, the evaluation of the new rosin derivatives available from Olustee research in the adhesive field was considered promising.

A contract was then entered into with Battelle Memorial Institute to evaluate our new materials in four areas of adhesives, namely:

Rubber tackifiers
Hot melts
Pressure-sensitive adhesives
Mastics

In all, a total of 42 carefully selected naval stores derivatives were prepared at the Naval Stores Laboratory for evaluation by Battelle; however, not all of the materials were tested in any one category.

The best products found in each area will now be described in terms of the following:

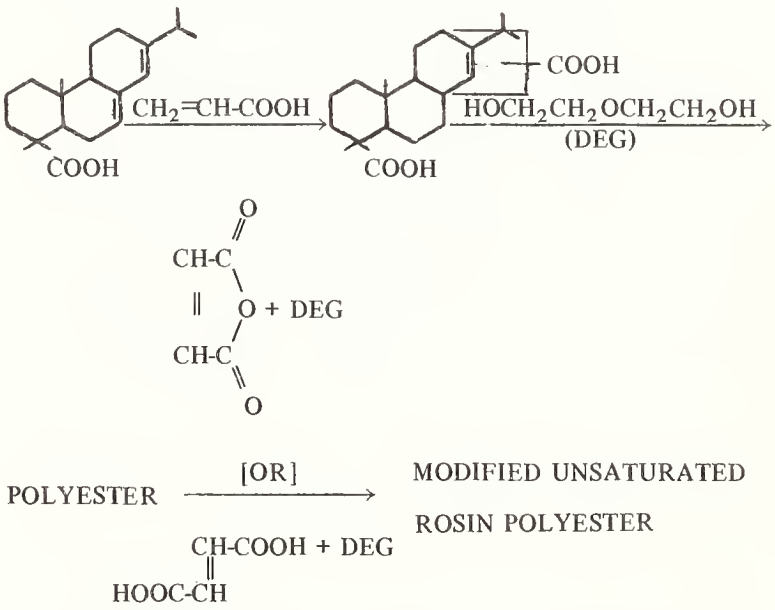
Softening point, ball and ring (S.P.)
Acid number (A.N.)
USDA rosin color grade
Materials cost
Process data

The materials costs are calculated on the basis of the following more or less arbitrary prices for the three types of rosin:

	Price per pound
Gum	$0.115
Wood.	.10
Tall Oil	.09

One product found active in three of the four areas under test is a rosin polyester. It is active in the areas: (a) rubber tackifiers, (b) pressure sensitive adhesives, and (c) hot melts. It was originally developed at Olustee for blending with styrene to give laminating resins. This work was pioneered by Halbrook, Lawrence, Dalluge, and Stein.[1]

The process for preparing the rosin polyester is indicated below:



The conjugated dienic acids of rosin are reacted with acrylic acid to give a dibasic acid via a Diels-Alder reaction. This dibasic acid is reacted with a glycol, in this case diethylene glycol (DEG), to give a polyester. This is called the unmodified polyester. This polyester can now be modified by reaction with more DEG plus maleic anhydride or more DEG plus fumaric acid to give a modified rosin polyester.

The properties of the rosin polyester modified with maleic anhydride are:

S.P.:	29° C.
A.N.:	60

[1] Indus. Engin. Chem., Prod. Res.Develpmt. 2, pp. 182-185. 1963.

Color grade: N

Materials cost:

Rosin:	Price per pound
Gum	$0.16
Wood	.155
Tall oil	.152

The properties of the rosin polyester modified with fumaric acid are:

S.P.: 38° C.
A.N.: 39
Color grade: N

Materials cost:

Rosin:	Price per pound
Gum	$0.175
Wood	.170
Tall oil	.167

The rosin polyester process in detail is as follows: Gum rosin is reacted with acrylic acid at 225° C. for 1.5 hours. Wood or tall oil rosin can also be used. However, in most of the work that has been carried out to date, gum rosin has been used. The dibasic acid adduct is then condensed with DEG at 275° to 280° C. for 6 hours to give the polyester. The relatively high temperature is required because of the hindered nature of the carboxyl group. The polyester can then be modified with maleic anhydride and more DEG by heating for 6 to 7 hours at 195° C. to give the maleic modified rosin polyester or the polyester can be modified by reacting it further with fumaric acid and DEG to give the fumaric acid modified rosin polyester.

Now that we have considered the most versatile product developed, we shall consider each of the four areas of adhesives in detail and consider the products found most active in each.

The first area we shall consider is that of rubber tackifiers. The first product on the list is the modified rosin polyester that we have just talked about. Research is still underway on the use of rosin polyester as tackifiers. A series of related materials has been prepared and is now being tested. The second product is maleic anhydride-modified pine gum, and the third is fumaric acid-modified pine gum.

The properties of maleic anhydride modified pine gum are as follows:

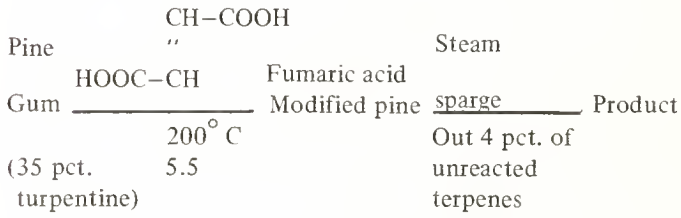
S.P.: 86° C.
A.N.: 350 (in acetone)
Color grade: K
Materials cost: $0.117 per pound

The process for the preparation of maleic anhydride modified pine gum is as follows: Commercial washed and cleaned pine gum containing 35 percent turpentine is reacted with maleic anhydride at 200° C. for 4.5 hours to give maleic anhydride modified pine gum. The product is steam sparged to remove 6 percent of unreacted turpenes and the resulting material is the final product. This reaction involved a Diels-Alder reaction of the rosin acids and terpenes with maleic anhydride.

The properties of fumaric acid modified pine gum are as follows:

S.P.: 112° C.
A.N.: 288 (acetone)
Color grade: WG
Materials cost: $0.12 per pound

The preparation of fumaric acid modified pine gum showing the Diels-Alder reaction with rosin and terpenes is as follows:



Pressure sensitive adhesives are next. Here again, the rosin polyester, modified with maleic anhydride or fumaric acid, is one of the most interesting products.

Next we will consider hot-melt adhesives. In this area, hydrogenated pine gum looked most interesting in poly-(vinyl acetate) formulations. The glycerol ester of fumaric modified rosin is of most interest in polyamide formulations. The rosin polyester (unmodified) looked most promising in ethylene-vinyl acetate formulations.

Hydrogenated pine gum has the following properties:

S.P.: 19° C.
A.N.: 127
Color grade: WG
Materials cost: $0.10 per pound for pine gum.

Hydrogenated pine gum is prepared as follows: Commercial diluted pine gum containing 35 percent turpentine is treated with 1 percent of 5 percent Palladium-on-carbon and hydrogenated for 2 hours at 200° C. and 4,500 p.s.i.g. to give a mixture of reduced resin acids and terpenes. The mixture is

steam sparged until a product containing 20 percent hydrogenated terpenes is obtained. This is the material that was used in the tests. We hope to evaluate a number of variables in this process. First of all, the steam sparge can be eliminated, or as much turpentine as desired can be sparged out. The less hydrogenated terpenes present, the higher the softening point. Also, the temperature can probably be lowered and the reaction time shortened. The pressure can undoubtedly be lowered, and very possibly hydrogenation at atmospheric pressure would give a product of quite similar properties.

The properties of the glycerol ester of fumaric modified rosin are as follows:

S.P.:	127° C.
A.N.:	22.3
Color grade:	WG
Materials cost:	

Rosin	Price per pound
Gum	$0.145
Wood	.132
Tall oil	.124

The process for the preparation of the glycerol ester of fumaric modified rosin is as follows: One mole of gum rosin, that is, 300 grams, is reacted with 0.26 mole of fumaric acid at 200° C. for 1.5 hours to give the adduct. This is esterified with sufficient glycerol to react with all of the carboxyl groups present at 275° C. for 5.5 hours to give the product of A.N. as indicated above.

The properties of the rosin polyester unmodified are as follows:

S.P.:	51° C.
A.N.:	8.8
Color grade:	N
Materials cost:	

Rosin:	Price per pound
Gum	$0.15
Wood	.139
Tall oil	.132

The preparation of unmodified rosin polyester is as follows: Rosin is reacted with acrylic acid at 200° C. for 3 hours to give a dibasic acid, which is esterified with DEG at 275° C. for 7.5 hours to give the product.

In the last area of mastics, the products that looked most interesting were as follows:

(1) Pot residue of heat-treated gum rosin

(2) Zinc resinate of formaldehyde modified rosin

The properties of the pot residue of the heat-treated gum rosin are as follows:

S.P.:	138° C. (Zinc salt, SP 148° C.)
A.N.:	83.5 (E.W. 672)
Color grade:	K
Materials cost:	Cost of type of rosin used.

The process for the preparation of heat-treated rosin is as indicated. Gum rosin is heated at 300° C. for 20 minutes. The heat-treated rosin is subjected to a vacuum distillation at about 40 mm. pressure or a steam distillation at atmospheric pressure to give a 22 percent yield of pot residue. Analytical data on this residue indicates that most of it consists of a monobasic acid dimer. The yields of pot residue from various types of rosin are as follows:

Rosin:	Percent
Gum	22
Tall oil	6
Wood A	9
Wood B	15

The rosin from the distillation is upgraded to a color of XA or better.

The properties of the zinc resinate of formaldehyde modified gum rosin are as follows:

S.P.:	132° C.
Color grade:	H
Materials cost:	

Rosin:	Price per pound
Gum	$0.118
Wood	.105
Tall oil	.096

The process for the preparation of the zinc resinate of formaldehyde modified rosin is as follows: Gum rosin is reacted with paraformaldehyde at 170° C. for 1 hour to give the hydroxymethylol adduct. This is reacted with about 10 parts of zinc oxide per 100 parts of formaldehyde adduct at 250 ° C. for 7.5 hours to give the product.

In conclusion, a total of eight new materials have been presented for your consideration as new naval stores products for the adhesives field. The modified rosin polyesters are the most versatile of the eight products presented.

QUESTION: When you said you used 10 parts formaldehyde, what was the ratio of formaldehyde to rosin?

DR. SCHULLER: Five parts formaldehyde to 100 parts rosin. Ten parts to 100 parts when zinc is used.

QUESTION: What factors were used in calculating the manufacturing costs as half-cents per pound?

DR. SCHULLER: I'll refer that to Dr. McSweeney. We worked these out with him last night.

DR. McSWEENEY: These were the lowest possible costs and were based on the highest production volume possible.

QUESTION: Did it include labor costs?

DR. SCHULLER: It was based on use of molten rosin (molten in tank car) and includes labor and all other costs.

QUESTION: What volume, approximately, are you talking about?

DR. McSWEENEY: The largest possible. Use the largest kettle available--5,000 pound.

DR. SCHULLER: Obviously the production costs would vary with the batch size. Smaller volume would be higher. Use of cold rosin would also add the cost of heating.

QUESTION: What order of reliability does Mr. McSweeney hold for these costs--100 percent, 200 percent, 300 percent?

DR. McSWEENEY: I would not care to comment on this. The estimates are the most rough you can make.

DR. SCHULLER: The values are at best approximate.

QUESTION: Can we have an idea of the performance of the materials?

DR. SCHULLER: This will be discussed in later papers. However, they are as good in some cases and superior to commercial products in others.

QUESTION: In the preparation of the polyesters and modified polyesters did you investigate the effect of changing the variables?

DR. SCHULLER: The variables are now being investigated. In the work reported we used 15 parts acrylic acid to 100 parts rosin. We are now moving up with the amount of acrylic acid. With the maleic anhydride the proportions used were 3 moles maleic anhydride to 1 mole rosin. We are now using 1, 2, and 3 moles of maleic anhydride and fumaric acid and investigating the variables. We are also investigating the use of less acrylic acid.

QUESTION: This was all done on a molar basis?

DR. SCHULLER: Yes, but with a 10-percent excess diethylene glycol. As the variables change the price changes. The less fumaric and acrylic acids needed, the cheaper the material will be.

QUESTION: In the process, did you say that additional DEG was added after the first adduct reaction?

DR. SCHULLER: Yes, the rosin carboxyl is hindered so the adduct is first prepared, then additional glycol added, and the reaction completed at a lower temperature.

QUESTION: How much excess DEG is added at this point?

DR. SCHULLER: Ten percent is the figure we have been working on. We are now investigating this variable.

COMMENT (R. V. LAWRENCE): The amount is limited by the amount that can be kept in the pot at 275°. We usually had to add a little more than the 10-percent excess.

QUESTION: You had enough hydroxyl left to esterify with DEG?

MR. LAWRENCE: Yes, but we added extra DEG.

QUESTION: Would the product perform differently with blends?

DR. SCHULLER: This is now under investigation. We should get a random distribution.

COMMENT: At 200° the rosin composition should be set.

DR. SCHULLER: Yes.

QUESTION: Will you comment on the reaction that takes place between the rosin and the formaldehyde?

DR. SCHULLER: We should get a Prins-type reaction. The resin is methylolated by addition to one of the double bonds. The resulting product enables us to use a higher level of zinc.

QUESTION: Has any work been done to substitute methacrylic acid for acrylic acid?

DR. SCHULLER: No, but we probably will.

QUESTION: Do you have any data on the color stability in hot-melt applications on storage? On time of heating?

DR. SCHULLER: This will be discussed in a later talk on hot-melts.

QUESTION: What grade of rosin was used in this work?

DR. SCHULLER: WG grade was used.

QUESTION: It was not clear whether the unmodified rosin polyesters were good for these applications. Were they?

DR. SCHULLER: Yes. The third item in the hot-melt listing was this product. It did show promise.

THE USE OF NOVEL ROSIN DERIVATIVES IN PRESSURE-SENSITIVE ADHESIVES

by

D. A. Berry
Battelle Memorial Institute
Columbus, Ohio

For many years rosin derivatives have been used as tackifiers in pressure-sensitive adhesive formulations. It has been estimated that pressure-sensitive adhesives represent about 10 percent of the total consumption of rubber-based adhesives. Almost all formulations require the use of an added tackifier, this quite often being a rosin derivative. Stabilized rosin esters, such as the pentaerythritol ester of hydrogenated rosin, are usually chosen as tackifiers. The most common use of pressure-sensitive adhesives is for flexible tapes. The tack, or instantaneous adhesiveness, must not exceed the internal strength or cohesion of the adhesive. These adhesives usually lack high strength since they must be relatively soft.

The search for better tackifiers is a continuous one. Thus, a screening-type program was devised to evaluate 13 novel rosin derivatives in natural, butyl, and styrene-butadiene rubber formulations. Three types of substrates were used. These were cellophane, polyester (Mylar), and polyethylene. In no case was a primer used, but the adhesive was applied directly to the untreated film substrate. Thus, it is felt that the numerical values from the testing procedures are minimum values and that the use of the appropriate primer would enhance these figures. Exact formulations are given in tables 1, 2, and 3.

Table 1.—Butyl rubber formulation

Rosin derivative to base rubber	0.10	0.20	0.40	0.60	0.80	1.0
Butyl 035 rubber	3	3	3	3	3	3
Vistanex LM/MS	3.5	3.5	3.5	3.5	3.5	3.5
Rosin derivative	.65	1.3	2.6	3.9	5.2	6.5
Chloroform	40.5	45.2	51.4	58.1	66.3	73.5

Table 2.—SBR rubber formulation

Rosin derivative to base rubber	0.10	0.20	0.40	0.60	0.80	1.0
Ameripol 4502 rubber	5	5	5	5	5	5
Vistanex LM/MS	1	1	1	1	1	1
Rosin derivative	.5	1	2	3	4	5
Chloroform	58.5	63	72	81	90	99

Table 3. Natural rubber formulation

Rosin derivative to base rubber	0.20	0.40	0.60	0.80	1.0	1.2
Pale crepe rubber	4	4	4	4	4	4
Vistanex LM/MS	1.2	1.2	1.2	1.2	1.2	1.2
Rosin derivative	.8	1.6	2.4	3.2	4.0	4.8
Chloroform	54	61.2	68.4	75.6	82.8	90

It is well known that when various rubbers are mixed with rosin derivatives at different levels of concentration and plots made of tack versus the rosin/rubber ratios, the resultant curves often show steep slopes with sharp maxima. Thus, it is necessary when evaluating any rosin derivative to determine

these inflection points so that optimum ratios can be used. Examples of such curves are shown in figures 1 and 2. The control used throughout the program, Pentalyn H, is shown in the first figure, whereas one

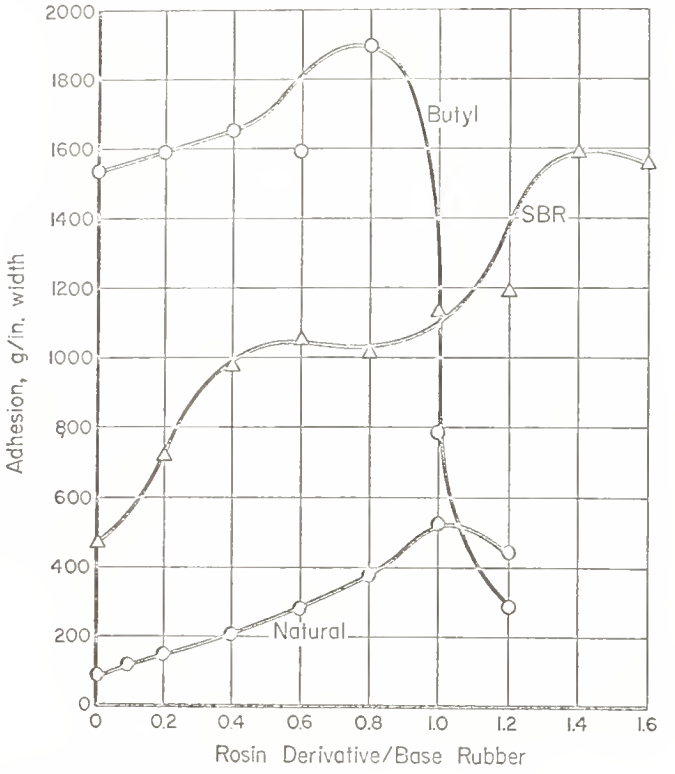


Figure 1.—Pentalyn H.

of the more promising candidate materials is shown in the second. One can immediately see by the shapes of these curves that gross differences occur when different rosin derivatives and rubbers are used. The

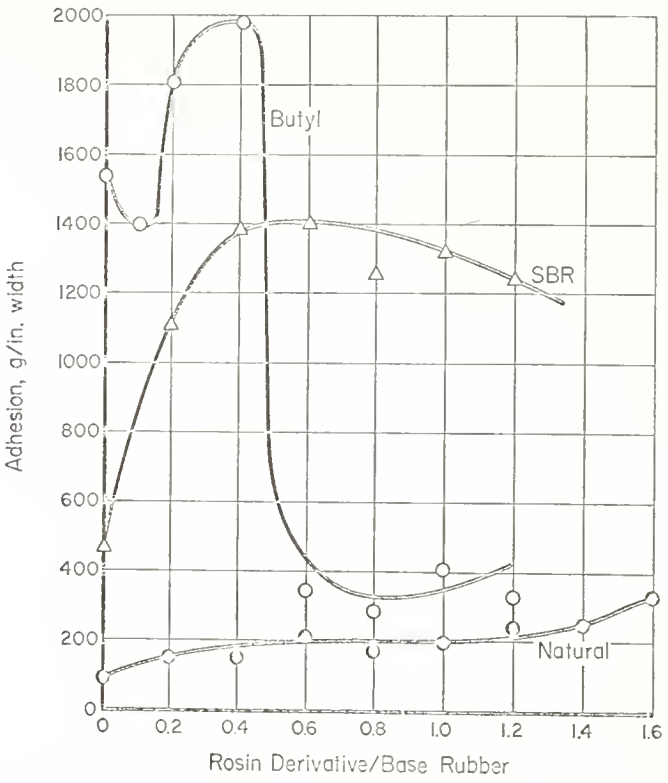


Figure 2.—Rosin-β-propiolactone adduct reacted with diethylene glycol and maleic anhydride.

adhesion was determined by applying the rosin rubber mixtures to cellophane, then using the T-peel test. These results are plotted as the vertical coordinate. The horizontal coordinate is the ratio of rosin to rubber. Thus, the point 1.0 is equivalent to equal parts of rosin to rubber.

Table 4 lists the 13 derivatives evaluated plus the pentaery-thritol control. Also shown in this table are

Table 4.—List of materials evaluated in pressure-sensitive adhesive formulations

Description	Ratio: Rosin / Rubber		
	Natural	Butyl	SBR
PE ester, hydrogenated rosin	1.0	0.8	1.0
Photoepoxidized pine gum	1.0	.1	.2
Dichlorocarbene adduct	1.0	.1	1.0
Oxonated rosin	.6	.1	.4
Gum rosin-CH_2O adduct	1.0	.2	.1
Rosin-BPL-DEG polyester[1]	.8	.1	.1
Rosin-BPL-maleic DEG polyester	1.0	.4	.1
Rosin-BPL-fumaric-DEG polyester	1.0	.1	.1
Fumaric-modified polyester	1.0	.1	.1
Disproportionated rosin-propylene oxide	1.0	.2	.6
Maleic-modified pine gum	.4	.1	.2
Fumaric-modified pine gum	.2	.2	.1
β-hydroxy ester	1.0	.1	.2
Diester of above	1.0	.8	1.0

[1] BPL = Beta-propiolactone.
DEG = Diethylene glycol.

the rosin/rubber ratios used for these derivatives as determined by the method described in the preceding paragraph. Each of these derivatives were evaluated using the T-peel and 180°-peel tests. Both of these tests are standard for pressure-sensitive adhesives.

The numerical data for the more promising materials along with the controls are given in tables 5 and 6. The blank is simply the rubber with no rosin

Table 5. – T-peel adhesion values for the more promising candidates and controls

	Adhesion (G/linear inch)								
	Cellophane film			Polyester film			Polyethylene film		
Formulation	SBR	Natural	Butyl	SBR	Natural	Butyl	SBR	Natural	Butyl
Blank	467	88	1539	774	50	1517	433	82	890
Pentaerythritol ester of partially hydrogenated rosin	1136	530	1894	1198	740	82	766	356	1743
Polyester (unmodified)	2316	459	1176	1524	113	858	1798	227	1144
Fumaric-modified polyester	1363	459	1705	1089	332	1126	1814	467	1544
Maleic-modified polyester	1398	200	1980	841	270	1199	1614	471	659

Table 6. – 180° peel adhesion values for the more promising candidates and controls

	Adhesion (G/linear inch)								
	Cellophane film			Polyester film			Polyethylene film		
Formulation	SBR	Natural	Butyl	SBR	Natural	Butyl	SBR	Natural	Butyl
Blank	1063	256	902	479	66	786	496	140	517
Pentaerythritol ester of partially hydrogenated rosin	1763	1051	713	1334	800	539	845	656	595
Polyester (unmodified)	855	476	869	817	293	1441	716	222	551
Fumaric-modified polyester	1270	435	1147	895	296	1044	866	261	755
Maleic-modified polyester	1117	661	932	845	415	1073	815	488	689

derivative added. The pentaerythritol ester of partially hydrogenated rosin is commercially available under the trade name Pentalyn H. The unmodified polyester was prepared from the addition product of beta-propiolactone and gum rosin as the dibasic acid component and diethylene glycol as the dihydric alcohol. An excess of about 10 percent glycol was used and the mixture reacted to obtain a product

having an acid number of about 30. This was also done with the materials labeled fumaric- and maleic-modified polyesters. However, in these cases the propiolactone adduct was used to supply about one-third of the carboxyl functionality and either maleic anhydride or fumaric acid was used to supply the remaining two-thirds. It can be seen that in almost every case the experimental derivatives were as good as or superior to the control. Although other materials showed promise in specific formulations, these three materials were the best overall.

Perhaps the most revealing evaluation was one involving accelerated aging of the various derivatives. These tests were carried out using Mylar film as the substrate. The aging was done at 158° F for 1 week and the tack then determined by T-peel. The results of this aging test are as follows:

Derivatives:	Effectiveness
PE ester, hydrogenated rosin	0.0
Photoepoxidized pine gum	28.1
Dichlorocarbene adduct	27.0
Oxonated rosin	71.4
Gum rosin-CH_2O adduct	39.8
Rosin-BPL-DEG polyester	4.0
Rosin-BPL-maleic-DEG-polyester	67.9
Rosin-BPL-fumaric-DEG polyester	77.7
Fumaric-modified polyester	10.7
Disproportionated rosin-propylene oxide	61.3
Maleic-modified pine gum	26.1
Fumaric-modified pine gum	47.5
β-hydroxy ester	73.0
Diester of above	2.0

The numbers represent the quotient from the division of the T-peel values after aging by those before aging multiplied by 100. It can be seen that the value of the control was zero after aging. The values of the maleic and fumaric polyesters were 67.9 and 77.7, respectively. This is of extreme importance since aging is one of the factors that must be given high priority by any adhesive manufacturer.

In summary, from the evaluation of 13 novel rosin derivatives, two looked extremely interesting in pressure-sensitive formulations. These are the fumaric- and the maleic-modified polyesters prepared from diethylene glycol and the adduct of gum rosin and beta-propiolactone. Fortunately, these materials would be relatively inexpensive. Also, the formulation of the polyesters could be widely varied by changes in the type of glycol used and the molar concentrations of the two dibasic acids.

DISCUSSION

QUESTION: As a representative of Hercules I wouldn't want to criticize your choice of control, but compliment you on your good judgment. I do have a question. First, did you age any of the tape before applying it to the substrate or was the aging strictly of the bonded material?

MR. BERRY: The aging was of the bonded material.

QUESTION: You have no data on the aging of the tape?

MR. BERRY: To my knowledge we do not. Have we, Al?

MR. A. BUNK: The materials were coated, then they were put in the oven and aged. They were put together for T-peel adhesion and were then pulled apart on the Instron.

QUESTION: How long were they aged?

MR. BUNK: They were aged 1 week at 70° C.

QUESTION: Is there any correlation between the softening point or the viscosity characteristics of the modifying resins with your performance?

MR. BERRY: No. We haven't made a direct correlation. When we started we had hoped to find a correlation between actual molecular structure and effectiveness of the material. This did not prove out. We have the softening point data, and anyone who tries to make this correlation, I'm afraid, will get thoroughly confused. When we get into these poly-

esters, it doesn't take very much drop in acid number and change in excess polyol to change the softening point.

QUESTION: When you were running the T-peel were you measuring adhesion to the backing of the substrate or were you measuring the cohesive strength of the adhesive? In other words, were you getting adhesive or cohesive failure during your T-peel test?

MR. BERRY: It depends on the adhesive. With some we definitely get cohesive failure. Ideally we would get adhesive failure. Of course this was not true. When we ran it on the Instron we got quite a fluctuation back and forth, a zig-zag pattern, you know, which we had to average out. These were signs of cohesive failure. When it starts to leg on you it really gets to be bad.

QUESTION: Did the adhesive stay with the film?

MR. BERRY: In most cases it stays with the substrate, except to sample started to leg.

QUESTION: On the 180° peel where did failure occur?

MR. BERRY: It was cohesion in most materials. The film and paper stayed with us with most materials in adhesive failure.

COMMENT: What happens when you pass the optimum resin/rubber ratio is that from that point on you have a continuous resin phase with a low molecular rubber in it rather than a continuous rubber phase with rosin in it.

QUESTION: Do you have any plans to extend this work to include acrylic-based pressure sensitives?

MR. BERRY: We included a commercial acrylic control and it looked quite good.

QUESTION: Are the rosin derivatives effective in acrylics?

MR. BERRY: We did not try the acrylic with the rosin. We simply got a commercial acrylic and applied it to the substrate to see what kind of value we would get. As I recall the adhesion values were about 700 to 800 p.s.i.

QUESTION: The question was, do you have any plans to extend this research to include acrylic based pressure sensitives?

MR. BERRY: Not within the present contract. Not in the immediate future. It would be nice work.

THE USE OF NOVEL GUM ROSIN DERIVATIVES AS RUBBER TACKIFIERS

by

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(Presented by W. J. Mueller)

When rubber is compounded to produce various products, it is a well established practice to add various additives to develop specific desirable properties. One such property is building tack, which is the ability of two pieces of unvulcanized rubber to adhere when brought together under pressure. This property is particularly important in such products as tires and belts where the component parts have to be assembled and held together until they can be vulcanized into a single unit. Between the time the parts are assembled and the product vulcanized, the assembly may be dropped on a conveyor belt, moved to temporary storage, removed from storage, and conveyed to the vulcanizing press, all with varying degrees of roughness. Failure of the various parts of a passenger tire, for example, to hold together through this process is obvious.

The first major question to be answered was how to evaluate a tackifier. There are no ASTM[1] or other standard tests. In the fall of 1965, the Rubber Division of the American Chemical Society held a symposium on building tack. While listening to these papers it soon became apparent that there were about as many ways of evaluating tackifiers as there were papers on the program. The technique that we have found to be very effective and used in this program was first described by Forbes and McLeod[2] of the Polymer Corporation at Sarnia. Basically, the test consists of compounding rubber compositions with all ingredients except curing agents and accelerators that tend to bloom to the surface. Small pellets are molded from these compositions, and they are held in contact under controlled conditions of time, temperature, and loading in an Instron Tester. They are then pulled apart at a constant rate and the force required to separate them is recorded. In addition to tack strength, it is desirable to determine the effect of tackifiers on other properties such as scorch time, curing, processing, and physical properties. Preferably, a tackifier should significantly improve tack strength and have little or no effect on other properties.

Because of our experience with this test in other programs, we knew that contact time was one of the most important variables in the test procedure. Tack strength usually increased significantly with contact time and we normally studied the range from half a minute to 60 minutes. Of course, the effect of the tackifier is important both at short and long contact times.

In setting up our program to screen materials as potential tackifiers, three polymers were chosen as typical of those to which tackifiers might logically be added. Styrene-butadiene polymer (SBR) was chosen because of its extensive use in tires. However, SBR-1006 prepared from fatty acid soap was chosen because it is known to have poor tack strength, and any effects from the tackifiers would be easier to spot. Butadiene-acrylonitrile polymers (called nitrile polymers) are used where good oil resistance is required, and a medium-high acrylonitrile polymer (Hycar 1042) was chosen as representative of this group. Ethylene-propylene-diene polymers (called (EDPM) present a special case, because past experience has shown wide variations between polymers both with respect to their tack strength and their response to the use of an added tackifier. Nordel 1070 was chosen as a typical polymer that has been found to respond well to the use of a tackifier.

Figure 1 shows the basic tack strength of the three polymers without added tackifier. SBR and nitrile

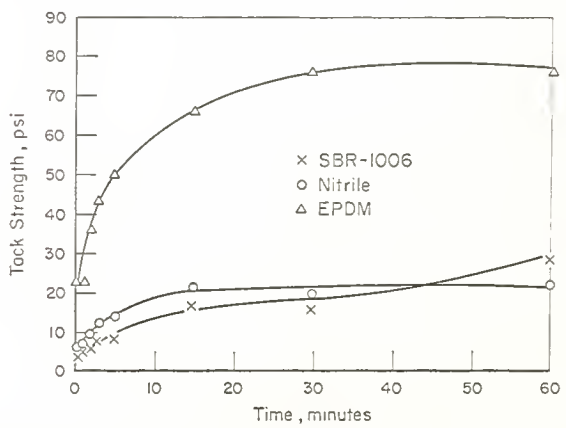

Figure 1.—Tack strength of polymers with tackifier.

[1] American Society for Testing Materials.

[2] Trans. Inst. Rubber Ind. **34**, No. 4, 154 (1958); Rubber Chem. Technol. **32**, 48 (1959).

rubber start at a very low level and increase slowly as the contact time increases. On the other hand, the EDPM started at a very much higher level, and rose to a level never reached by SBR and nitrile rubber even with added tackifiers. It is also important to note that we constantly ran controls in this program, which were compositions without added tackifier. The SBR and EDPM controls were very reproducible, while the nitrile rubber controls were not, as I shall show later.

Without doubt, the greatest volume of tackifier is used in SBR, so that studies with this polymer were given a heavy emphasis. Figure 2 shows data obtained with two modified polyesters (which are identified as items A and B on the attached sheet). The improvement in tack strength showed up over the whole range of contact times and represents some of the best data obtained with SBR. The maleic derivative was better than the fumaric, which we have consistently observed throughout our work.

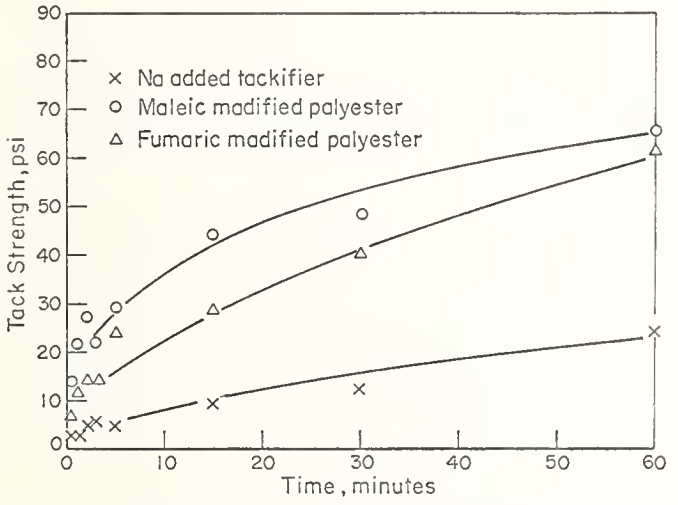

Figure 2.–Effect of tackifier on SBR with two modified polyesters.

Figure 3 compares two maleic modified materials, the polyester (item B) and gum (item F). Here again, the polyester was more effective than the pine gum.

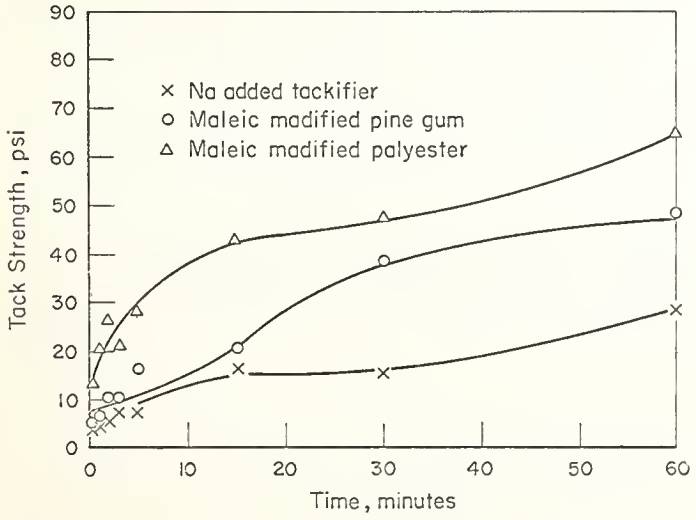

Figure 3.–Effect of tackifier on SBR with two maleic modified materials.

Figure 4 shows a rather different type of behavior when we compare a commercial pine gum with a fumaric modification (item E).

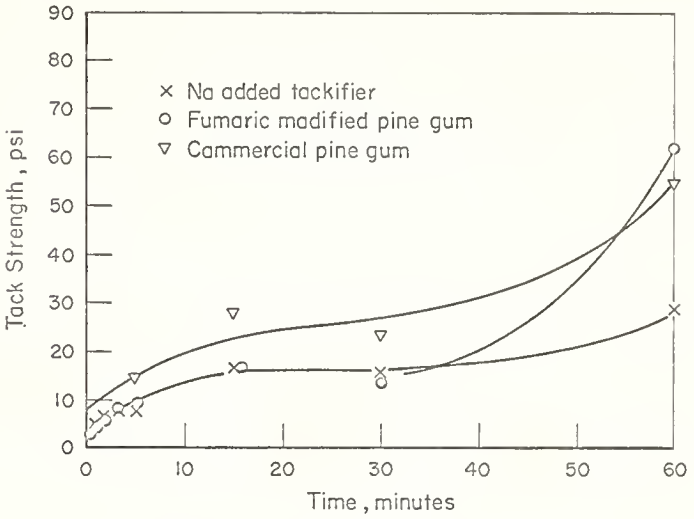

Figure 4.–Effect of tackifier on SBR with a commercial pine gum and a fumaric modification.

The fumaric modified pine gum showed no advantage except at the longest contact time. This type of behavior was shown by several materials investigated in this program.

Now, the data shown in the previous figures were all obtained using five parts of tackifier per hundred parts of rubber. Figure 5 shows the effect of varying the concentration of the maleic modified polyester. This figure shows that the tack strength increases nicely with concentration, as you would predict that it might. Some data, which I will show later, did not turn out as nice and neat as this.

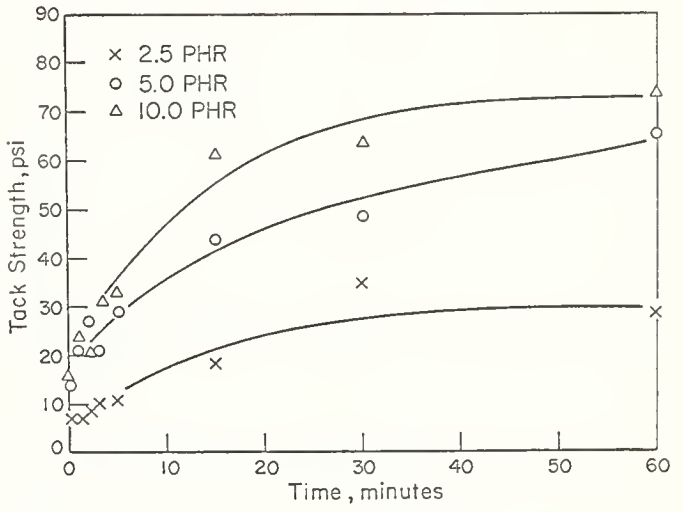

Figure 5.--Effect of tackifier concentration in SBR-maleic modified polyester.

In figure 6 we start showing the effects of tackifiers with nitrile rubber. This shows that the unmodified polyester (item D) and oxonated rosin

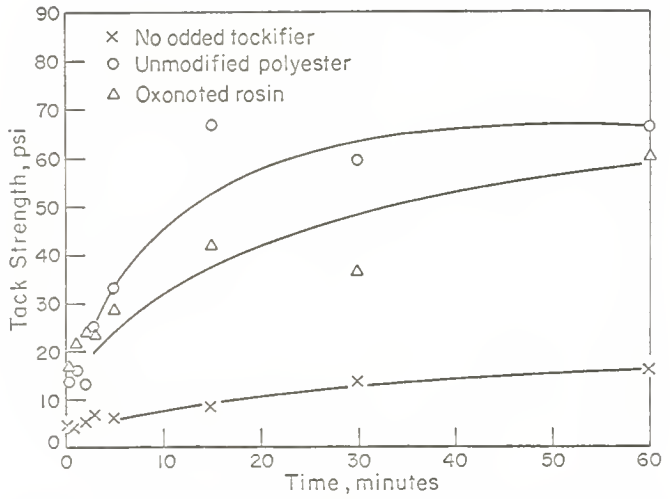

Figure 6.–Effect of tackifier in nitrile rubber with unmodified polyester and oxonated rosin.

(item G) greatly improved the tack strength over the whole range.

Another very good material was the disproportionated rosin reacted with propylene oxide (item H) as shown in figure 7.

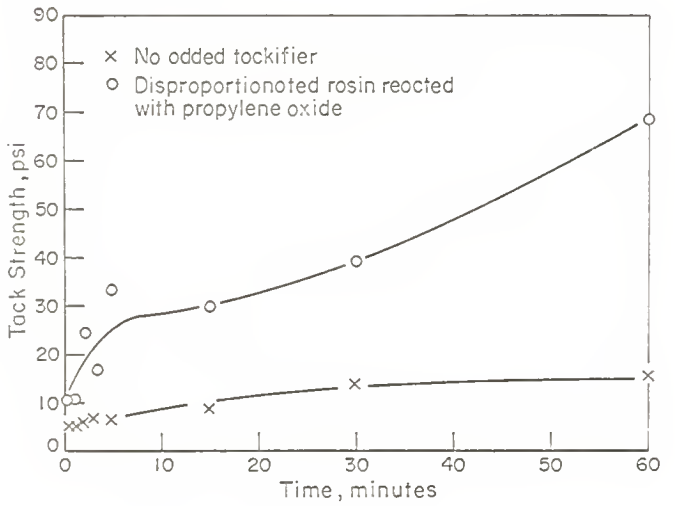

Figure 7.–Effect of tackifier in nitrile rubber with the disproportionated rosin reacted with propylene oxide.

Figure 8 shows both the result on a new material and one of the problems with this type of work. The earlier figures with nitrile rubber showed the control

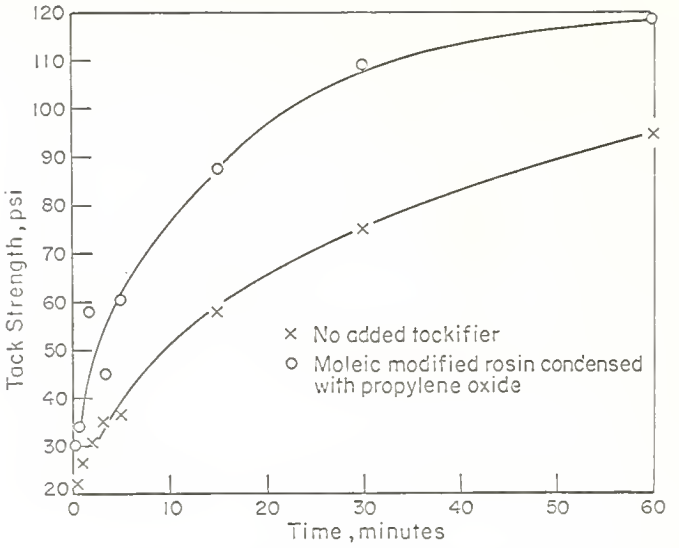

Figure 8.–Effect of tackifier in nitrile rubber with maleic modified rosin condensed with propylene oxide.

with no tackifier to end up at about 30 p.s.i. At this point we obtained a new batch of Hycar 1042, and you can see what happened to the control. However, the maleic modified rosin with propylene oxide (item R) still showed a significant improvement and actually had the highest tack strength we have ever recorded.

Figure 9 showing the results obtained with the two pine gum samples again shows, as in the case of SBR, that they are effective at long contact times, but have limited value at short contact times.

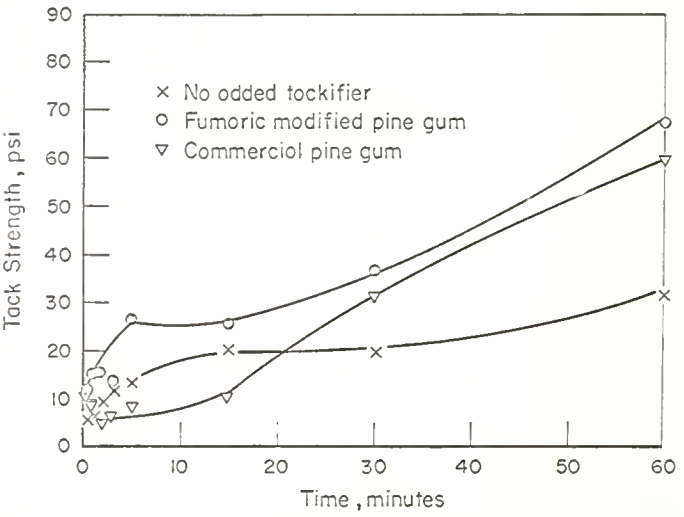

Figure 9.–Effect of tackifier on nitrile rubber.

Figure 10 shows the effect of tackifiers concentration using the maleic modified polyester. The concentration effect was much less pronounced than it was

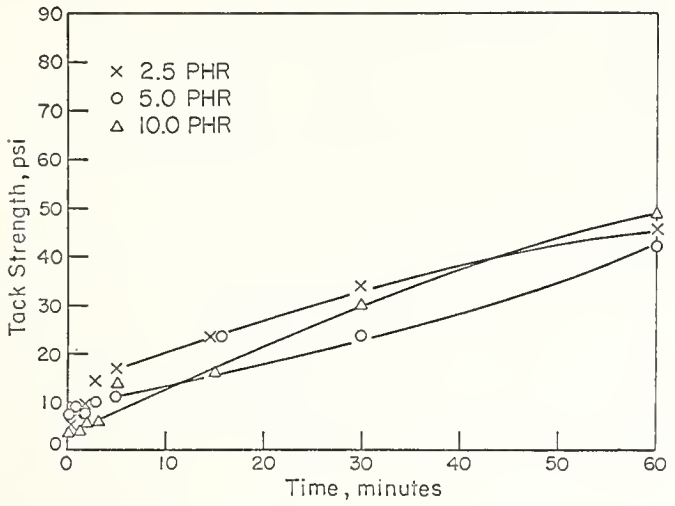

Figure 10.–Effect of tackifier concentration in nitrile rubber-maleic modified polyester.

with SBR. In fact, from the way these lines cross, you have to conclude that there is no really significant effect.

Now, the third polymer with which we worked with EDPM. Figure 11 shows that the control without added tackifier eventually reached a tack strength of about 75 p.s.i. Both the formaldehyde modified rosin (item I) and the maleic modified rosin condensed with propylene oxide (item R) added 10 to 15 p.s.i. over the whole range of contact times.

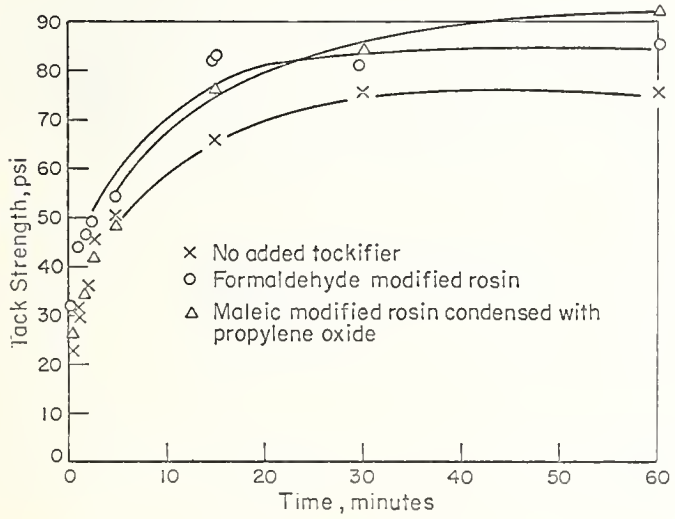
× No added tackifier
○ Formaldehyde modified rosin
△ Maleic modified rosin condensed with propylene oxide
Tack Strength, psi
Time, minutes

Figure 11.–Effect of tackifier in EPDM with formaldehyde modified rosin and maleic modified rosin condensed with propylene oxide.

Figure 12 shows the effect of the two polyesters. The maleic modified material improved the tack

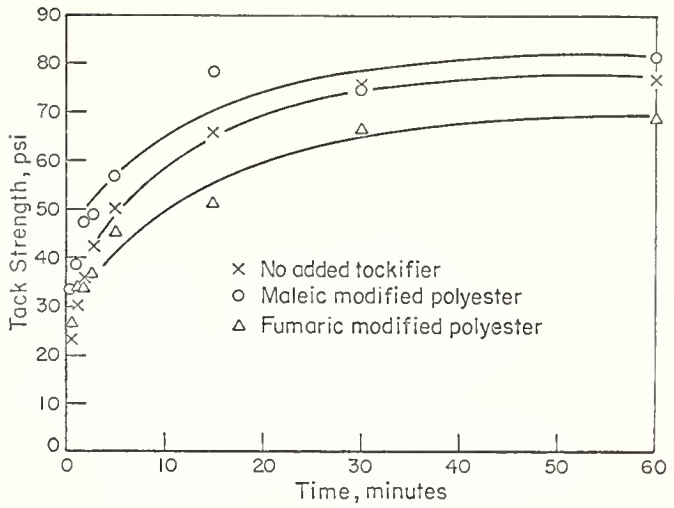

Figure 12.–Effect of tackifier in EPDM with two polyesters.

strength about 5 p.s.i., whereas the fumaric modified material produced a composition about 10 p.s.i. poorer than the control over the range of contact times.

Figure 13 shows typical data on the effect of tackifier concentration in EDPM. In this case, we show the data obtained with fumaric modified pine

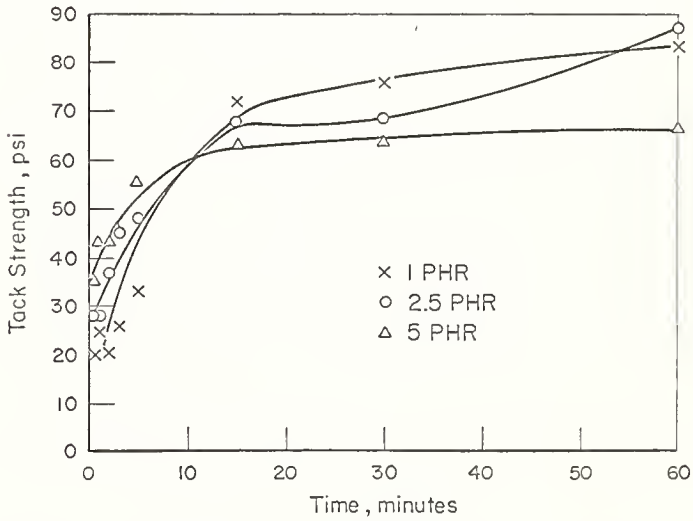

Figure 13.–Effect of tackifier concentration-fumaric modified pine gum in EPDM.

gum. At the short contact times, increasing tackifier concentration increased tack strength. At about 10 minutes contact time, the curves crossed over, and at long contact times, the lowest tackifier concentration was most effective. Thus, we have shown that the three polymers responded in different ways to changes in the tackifier concentration.

Now, the first 13 figures have dealt entirely with the subject of tack strength. At the beginning of my talk, I mentioned that a good tackifier should have little or no effect on other properties. This effect has

been examined only in SBR, and the next three tables will show some of these results.

A major concern of every rubber compounder is the effect of any additive on scorch and cure properties. Scorch refers to premature partial vulcanization of a rubber composition during hot processing and before it is ready to be cured. Scorch and cure properties are conveniently measured in a Mooney viscometer. This instrument measures relative viscosity at any temperature. When a sample in the instrument is subjected to a shearing force, the viscosity first decreases as the sample warms up. Viscosity then increases as curing begins. A convenient test is to measure the time required for the viscosity to rise 5 units above the minimum as an indication of scorching, and 35 units above the minimum as an indication of curing. Table 1 illustrates this behavior. Data at 250° F, which simulates a typical hot processing temperature, shows that the composition without added tackifier took 49 minutes to begin to scorch, while the addition of maleic modified polyester increases this to 56 minutes, which really means another 7 minutes of added safe processing time. At the curing temperature of 302°F, the most significant value is the 035-05 time, since this is an indication of cure rate. Both compositions are essentially equal, indicating equal rates of cure. At each temperature, the minimum viscosity was lower with the tackifier added, which would make processing easier. In other words, the maleic-modified polyester acted as a plasticizer that increased the scorch time 7 minutes but did not retard the curing rate. All three of these effects are highly desirable.

Table 1.–Effect of tackifier (maliec modified polyester) on scorch and cure properties of SBR-1006 compositions

Tackifier	None	Maleic modified polyester
Mooney scorch and cure data at 250° F.:		
Minimum viscosity	44	37
Δ5 minutes	49	56
Mooney scorch and cure data at 302° F.		
Minimum viscosity	46	36
Δ5 minutes	7.4	8.4
Δ35 do	10.3	11.5
Δ35-Δ5 do	2.9	3.1

By contrast, table 2 shows the effect of using a commercial pine gum. This additive also acted as a plasticizer, which increased scorch time. However, it

Table 2.–Effect of tackifier (commercial pine gum) on scorch and cure properties of SBR-1006 compositions

Tackifier	None	Commercial pine gum
Mooney scorch and cure data at 250° F.:		
Minimum viscosity	44	36
Δ 5 minutes	49	59.5
Mooney scorch and cure data at 302° F.:		
Minimum viscosity	46	34
Δ5 minutes	7.4	7.7
Δ35 do	10.3	13.8
Δ35-Δ5 do	2.9	6.1

most than doubled the 035-05 time, which means that it significantly retarded the curing, which is highly undesirable.

Table 3 shows the effect of the two tackifiers on some of the basic physical properties. The modulus is

Table 3.–Effect of tackifier on physical properties of SBR-1006 vulcanizates

Tackifier		None	Maleic modified polyester	Commercial pine gum
100 percent modulus	p.s.i.	280	220	130
300 percent modulus	do	1240	920	480
Tensile strength	do	2520	2720	1230
Elongation	percent	520	620	660
Hardness, shore A-2		62	64	55
Compression set,				
22 hour	percent			
158° F.		8	9	11
212° F.		16	17	18

Cure: 30 minutes at 302° F.

a measure of the force required to stretch the material to a given elongation, and it is seen that both tackifiers significantly reduce the modulus. The commercial pine gum also lowered the tensile strength and a composition with a much lower hardness. Surprisingly, neither tackifier had much effect on compression set properties.

To summarize, tackifiers were examined in three polymers and the following observations can be made from the results of the study:

1. The basic tack strength of the three polymers varied widely.
2. The optimum tack strength was obtained using different materials with each polymer. With SBR, the maleic modified polyester was most effective (item B). In nitrile rubber, the unmodified polyester, oxonated rosin, and maleic modified rosin condensed with propylene oxide were most effective over the whole range of contact times (items D, G, and R). At long contact times, the two pine gums (items E and F) were very effective. In EPDM, the formaldehyde modified rosin, maleic modified polyester, and the maleic modified rosin condensed with propylene oxide (items B, I, and R) were the best of the materials evaluated.
3. The effect of tackifier concentration was different with each polymer.
4. The tackifiers can have an undesirable effect on properties such as curing rate. Such an effect will be just as important as ability to improve tack strength when determining the commercial potential of these materials.

PINE GUM AND ROSIN DERIVATIVES SHOWING PROMISE

Code letter	PRESSURE-SENSITIVE ADHESIVES	Softening point °C.
A	Fumaric-modified polyester	38
B	Maleic-modified polyester	29
C	Disproportionated diester of the beta-hydroxy ester of rosin (Rosin Nedox 1518 diester)	36.5

Code letter	RUBBER TACKIFIERS SBR Composition	Softening point °C.
A	Fumaric-modified polyester	38
B	Maleic-modified polyester	29
	Butadiene-Acrylonitrile Rubber	
D	Polyester	49
E	Fumaric-modified pine gum (hydrogenated)	121
F	Maleic-modified pine gum (hydrogenated)	101
G	Oxonated rosin	98
H	Disproportionated rosin reacted with propylene oxide	34
R	Maleic-modified rosin condensed wtih propylene oxide	53
	EPDM Composition	
B	Maleic-modified polyester	29
I	Formaldehyde-modified rosin	98.5
	HOT-MELT ADHESIVES **Polyamide**	
J	Glycerol ester of fumaric-modified rosin	126
K	Disproportionated beta-hydroxy ester of rosin (Rosin Nedox 1518 monoester)	[1]
	Ethylene-Vinyl Acetate	
D	Polyester	49
L	Diethylene glycol ester of fumaric-modified rosin	55
M	Hydrogenated pine gum	19
	Polyvinyl Acetate	
M	Hydrogenated pine gum	19
F	Hydrogenated maleic-modified pine gum	101
G	Oxonated rosin	98
	MASTICS **Reclaimed Rubber**	
N	Residue from the distillation of gum rosin	138
O	PE ester of the residue from the distillation of gum rosin	137
P	Zinc salt of the residue from the distillation of gum rosin	148
Q	Zinc resinate of formaldehyde-modified rosin	132
	SBR or Natural Rubber	
Q	Zinc resinate of formaldehyde-modified rosin	132

[1] Gardner bubble viscosity, Z4.

QUESTION: Was any control run on the time, after milling, before the two pieces of rubber were pressed together?

MR. MUELLER: Normally these were milled one day and remilled the second day, then molded the second day. It wasn't closely controlled, but I would say it was normally within a couple of hours. It certainly wouldn't be over 2 to 3 hours at the most.

QUESTION: Was any aging study made on the milled stock?

MR. MUELLER: No. We have done a limited amount of this type of work in connection with some other research. It is another variable and cannot be ignored. There is no question that aging has a strong effect on tackifiers. It definitely affects tack strength.

QUESTION: Was the time reported the internal samples were held together?

MR. MUELLER: Yes. They were held under pressure in the Instron for the prescribed time, then pulled apart.

QUESTION: Was any comparison made with other standard rubber tackifiers such as the phenolics or coresins?

MR. MUELLER: We had very little opportunity to do so. Our sample supply was limited. This was a screening program in which we compared one experimental material against another. It would be difficult to determine which commercial tackifiers to compare against. Industry uses a wide variety of materials.

QUESTION: Was a tack-retention time study made?

MR. MUELLER: No. We did not have this opportunity. We expect the retention time to affect the tack.

QUESTION: When you were comparing nitriles you noted two substantial differences. What conclusions have you drawn?

MR. MUELLER: Only that various batches performed differently. The material we purchased at this time was different from the material we had been using. It could have been that the company had changed the manufacturing process, or the product changed with aging, or some other fact. The only thing we know for certain is that it was a different batch of material. This points out the importance of running these controls constantly and one way we had considered reporting these, an alternate method of reporting the data, would be to report these values as percent of the value obtained with the control containing no tackifier. This will minimize this effect of control.

We know the EPDM polymers today are different from 5 years ago. Why? We don't know. We do know the tack strength is different and this could apply to other problems, I'm quite sure.

QUESTION: You described using a disproportionated rosin. Was it a control?

MR. MUELLER: We used Galex NXD as a control. There was also a disproportionated material used in an experimental sample. It looked quite good.

HOT-MELT ADHESIVES – A PROGRESS REPORT

by

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INTRODUCTION

The Southern Utilization Research and Development Division of the United States Department of Agriculture is interested in expanding the use of gum rosin, and pine gum and their derivatives. Because of this interest, work was initiated to evaluate the potential of materials in adhesives. One area of emphasis was hot-melt adhesives.

Approximately 20 rosin derivatives are being evaluated as additives to hot-melt formulations. The program is designed to provide preliminary screening data. In no instance will a screening formulation be considered optimum. However, even the preliminary results show promise for this type of application.

EXPERIMENTAL WORK

Evaluation procedures – The effect of the use of a gum rosin or pine gum derivative in a hot-melt adhesive formulation after application to a substrate is being determined by measuring adhesion, wettability, flexibility, and block resistance. The viscosity of the hot-melt formulation is determined before and after a heat-stability test at a shear rate of 835 $secs^{-1}$.

Samples prepared for adhesion values are laminated in a Preco press at 300° F., 100 p.s.i., for 10 seconds. The samples are placed between two stainless steel plates of 1/8-inch thickness. Two sheets of 10-mil Teflon are used between the stainless steel plates and the samples. This is done to aid in removal of samples should hot-melt adhesive get on the plates during lamination. The adhesion values of the adhesive bonds are then evaluated using ASTM[1] Method D903-49, except that the number of test specimens is reduced to two.

Hot-melt adhesive formulations – The initial formulations come from trade literature. The polyamide and polyvinyl acetate formulations had to be modified to obtain adequate adhesion to a polyester film substrate. A list of the formulations and the concentrations of rosin derivatives being used can be found in table 1.

[1] American Society for Testing Materials.

Table 1.–Hot-melt adhesive formulations

System	Parts by weight		
Polyamide:	10 phr [1]	15 phr	20 phr
Emery 3749	50	50	50
Rosin derivative	5	7.5	10
Sunoco wax 3425	2.5	2.5	2.5
Ethylene-vinyl acetate:	50 phr	75 phr	100 phr
Elvax 150	40	40	40
Sunoco wax 5825	30	30	30
Rosin derivative	20	30	40
Polyvinyl acetate:	25 phr	50 phr	75 phr
Gelva V-21/2	25	25	25
Velva V-15	25	25	25
Rosin derivative	12.5	25	37.5
Santicizer B-16	25	25	25

[1] phr= parts of rosin derivative per hundred parts of base resin.

Adhesion values – The method used for testing adhesion is intended to determine the comparative peel or stripping characteristics of adhesive bonds. The adhesion value is the average load per unit width of bond line required to separate progressively one member from the other over the adhered surfaces at a separation angle of approximately 180° and at a separation rate of 12 inches per minute jaw speed.

The first step in evaluating each rosin derivative is to check the effect of varying the concentration. Each rosin derivative is used in three concentrations. The formulation that has adhesion values comparable to or better than a blank formulation (no rosin derivative) on a polyester film substrate is then evaluated on a 40-pound kraft liner board and in a laminate specimem consisting of the 40-pound kraft liner board and a pure aluminum foil. The peel strength of the hot-melt adhesive is determined again on a polyester film substrate after the heat-stability test is run.

Heat stability – Hot-melt adhesives should be stable over long periods of heating. Their viscosity and color should change little during this period. The heat stability of the hot-melt adhesives is determined by holding the formulations for 18 hours at the temperature at which they were prepared. The polyamide and ethylene-vinyl acetate formulations are being run at 280° F. while the polyvinly acetate formulation is being held at 350°.

SUMMARY

Work done thus far indicates that a number of rosin derivatives show promise in each hot-melt adhesive system. The overall performance of the blank formulation appears to be as good and in many cases better than the performance of formulations containing a water-white gum rosin or a rosin derivative. The trade literature formulation and a control using the pentaerythritol ester of a partially hydrogenated rosin had overall performances somewhat less for each hot-melt adhesive system. Taking into consideration the overall performance of the rosin derivatives in the formulations at the present time, the following appear to show promise:

Polyamide formulation:

(1) Glycerol ester of fumaric-modified gum rosin

(2) Disproportionated beta-hydroxy ester of gum rosin

Ethylene-vinyl acetate formulation:

(1) Gum rosin beta-propiolactone adduct reacted with diethylene glycol (polyester)

(2) Diethylene glycol ester of fumaric-modified gum rosin

(3) Hydrogenated pine gum

Polyvinyl acetate formulation:

(1) Hydrogenated pine gum

(2) Hydrogenated maleic-modified pine gum

The above promising materials are listed in their order of performance, with the (1) items performing as well as or better than the blank.

QUESTION: Am I right in assuming the oven-aged values on adhesion were on oven aging of the melt?

MR. BUNK: Yes, these were aged in an oil bath applied to substrate, conditioned, and evaluated.

QUESTION: Do you have any data on the aging of the bond?

MR. BUNK: No.

QUESTION: Did you record any color changes during the aging?

MR. BUNK: Yes. All the formulations darkened to various degrees.

QUESTION: Did you measure creep?

MR. BUNK: No.

QUESTION: Did these recipes contain any stabilizer?

MR. BUNK: No.

COMMENT: This could explain the viscosity and color values.

MR. BUNK: Yes, if you had a stabilizer and/or an antioxidant, the viscosity and color values should be better.

QUESTION: You talked about using these materials in hot-melt adhesives for the packaging field. However, you tested at 280° F. This is 70° too low for such use. The test should run about 100 hours at 350° F. Many materials will stand up for extended periods at 280° and fall apart rapidly at 350° F. Are you aware of this?

MR. BUNK: Yes, we were.

QUESTION: Were the results you reported on single samples or duplicates?

MR. BUNK: These were the averages of duplicates.

QUESTION: Did you study the compatibility of these derivatives with ethylene vinyl acetate?

MR. BUNK: We had no trouble in compatibility with the experimental materials we evaluated. There could be problems of compatibility with polyvinyl acetate. One of our controls was incompatible in this type formulation.

THE USE OF NOVEL ROSIN DERIVATIVES IN RUBBER-BASED MASTICS

by

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Three solvent rubber-based mastic formulations were used for evaluating the rosin derivatives. Each rosin derivative was used at three concentrations and evaluated in a reclaimed, natural, and styrene-butadiene rubber (SBR)-based mastic. All evaluations were made on a plywood substrate. Each formulation was evaluated for open time, green tack strength, lap-shear strength before and after aging, embrittlement after aging, and resistance to a static load at an elevated temperature.

A total of 19 rosin derivatives were evaluated in a reclaimed rubber mastic, 14 in a natural rubber mastic, and 16 in a SBR mastic. A typical formulation used in the evaluation program is given in table 1.

Table 1.–Typical mastic formulation

Ingredient	Parts by weight (150 phr)[1]
Reclaimed rubber (Naugatuck No. 662)	16.39
Rosin derivative	24.69
Dixie Clay	8.23
Calcene TM	8.23
Asbestos 7T06	8.23
Neozone D	0.24
Toluene	15.30
n-Hexane	18.70

[1] 150 parts rosin derivative per hundred parts of rubber. Mastics also prepared at 125 and 175 phr.

Lap-Shear Results

In a reclaimed rubber-based mastic, four rosin derivatives of the 19 evaluated produced outstanding adhesion on plywood. Each, when evaluated at three concentrations, had one or more formulations that compared favorably in adhesion performance to commercial SBR-type mastics. The adhesion values for these range from 143 to 254 p.s.i., compared with 208 to 230 p.s.i. for commercial mastics used as controls. The four rosin derivatives are: (1) the residue from the distillation of gum rosin, (2) the pentaerythritol ester of the residue from the distillation of gum rosin, (3) the zinc salt of the residue from the distillation of gum rosin, and (4) the zinc resinate of formaldehyde-modified rosin. After aging, the adhesion values generally decreased. Two exceptions were the low-concentration formulation using the residue from the distillation of gum rosin, which remained the same, and the zinc resinate of formaldehyde-modified rosin, also at the low concentration, which showed an increase in adhesion of approximately 40 percent. Three other formulations evaluated had adhesion values after aging that were substantially greater. These contained rosin anhydride, the ethylene glycol ester of fumaric-modified rosin, and the ethylene glycol ester of maleic-modified rosin. Many of the formulations of this group showed a twofold increase in adhesion on aging. The values ranged from 100 to 209 p.s.i.

Only one rosin derivative of the 14 evaluated in a natural rubber-based mastic led to a formulation with values before and after aging that were high enough to merit mention. This was the high-concentration formulation of the zinc resinate of formaldehyde-modified rosin. An average value of 190 p.s.i. was obtained before aging. This decreased to 167 p.s.i. after aging. A second derivative, the glycerol ester of

fumaric-modified rosin, had good adhesion in natural rubber-based mastics before being aged. Values from 150 to 200 p.s.i. were obtained. Aging caused complete loss of adhesion.

Of the 16 rosin derivatives evaluated in an SBR-based mastic, none were better for adhesion than the control formulations. When evaluated in this type mastic, the zinc resinate of formaldehyde-modified rosin showed values ranging from 109 to 145 p.s.i., whereas those for the controls ranged from 86 to 168 p.s.i. Several formulations increased significantly in adhesion after aging. These contained the zinc resinate of formaldehyde-modified rosin, rosin anhydride, the diethylene glycol ester of fumaric-modified rosin, and the gum rosin beta-propiolactone adduct reacted with diethylene glycol. Some of the values obtained with these formulations were in the range of those for the commercial mastics. The lap-shear values of the more promising materials are given in figures 1, 2, and 3.

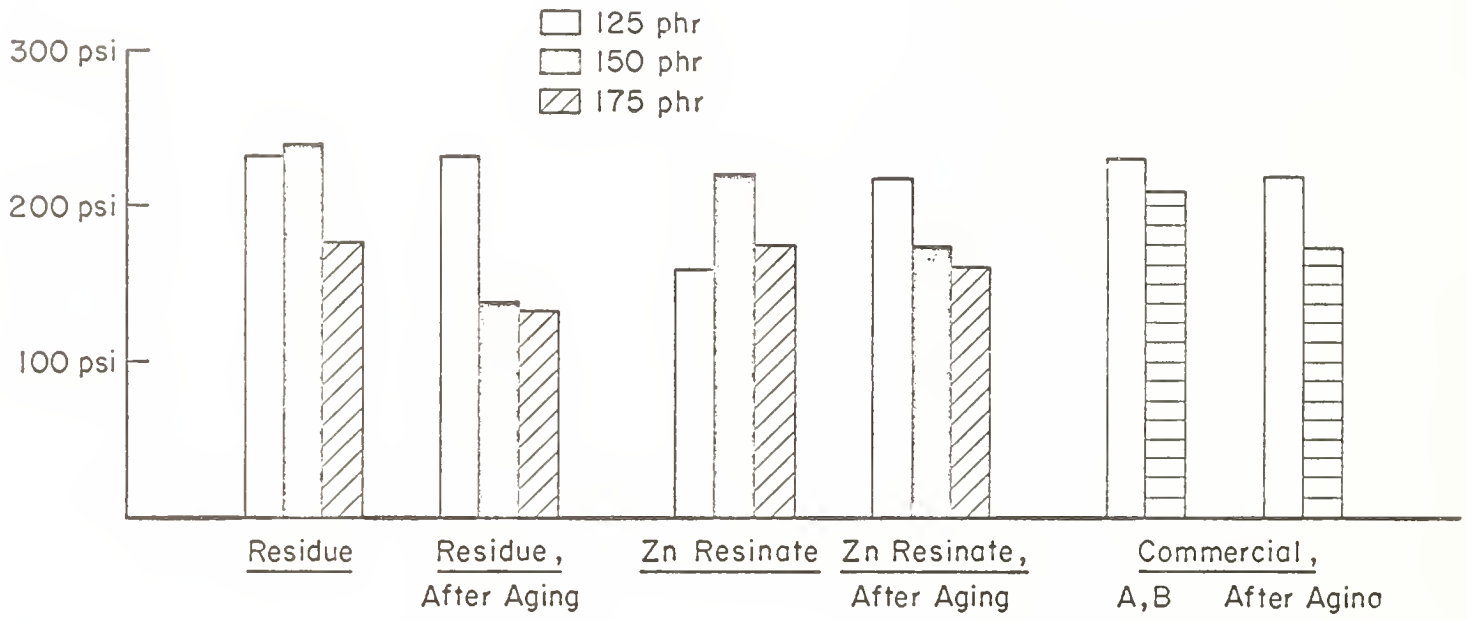

Figure 1.—Lap-shear strengths of reclaimed rubber-based mastics.

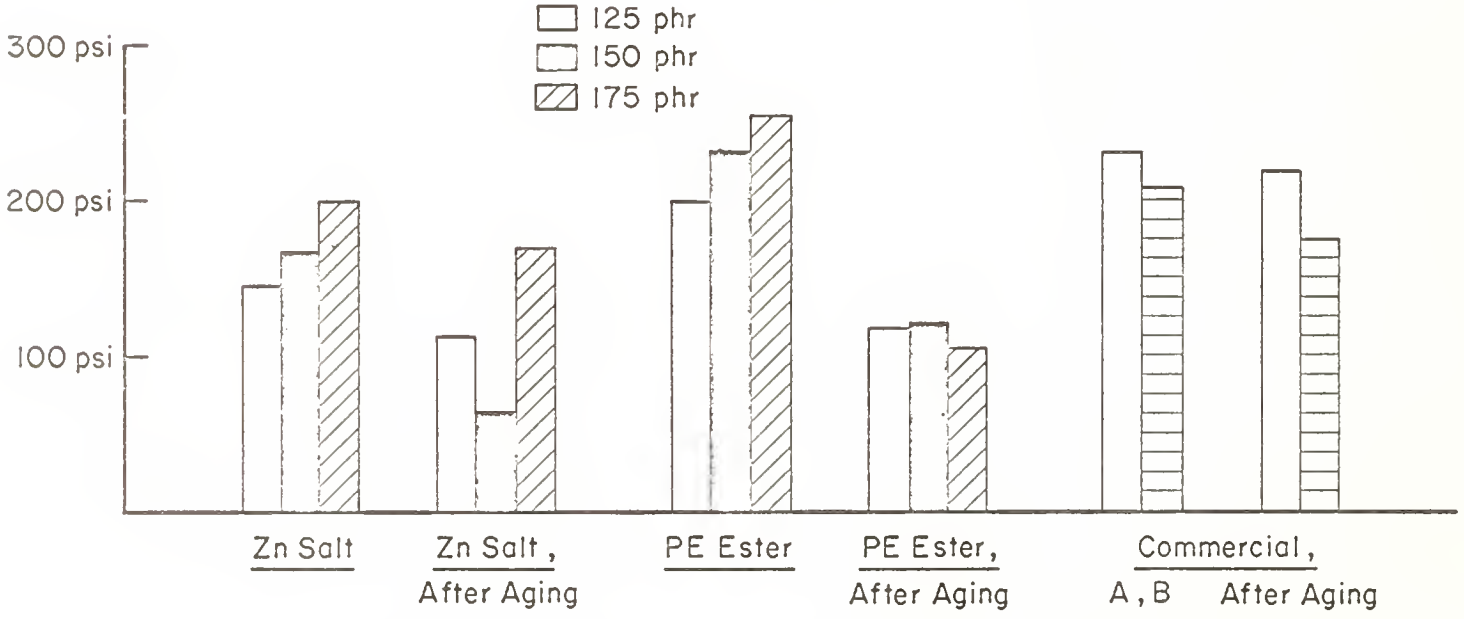

Figure 2.—Lap-shear strengths of reclaimed rubber-based mastics.

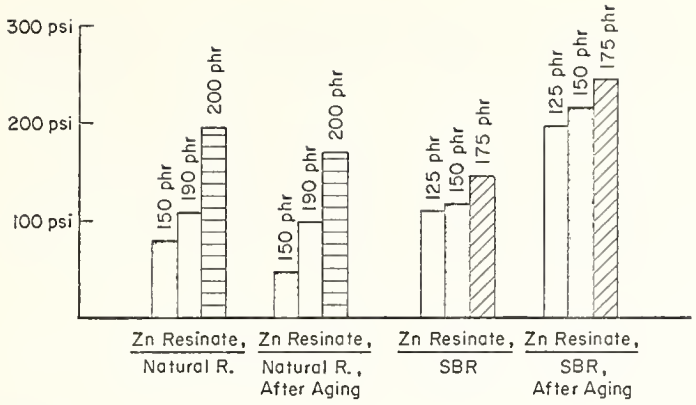

Figure 3.—Lap-shear strengths of natural rubber and SBR-based mastics.

Resistance to Embrittlement After Aging

The amount of embrittlement occurring during the accelerated aging test was measured as the percent deformation occurring in the aged specimen as compared with that of the room-temperature specimen. These values are given in table 2.

Table 2.—Resistance to embrittlement after aging[1]

Specimen	Deformation
	Pct.
Residue in reclaim mastic	80
Zn resinate in reclaim mastic	61.7
Zn salt in reclaim mastic	54.2
Penterythritol in reclaim mastic	37.5
Zn resinate in natural rubber mastic	66.7
Zn resinate in SBR mastic	36.5
Commercial mastic A	80.8
Commercial mastic B	53.4

[1] For phr of derivative corresponding to maximum unaged lap-shear strength.

Mastics using reclaimed rubber – In a reclaimed rubber-based mastic, three formulations had only slight embrittlement, three others became more elastic, and six formulations along with the gum rosin and commercial controls became more brittle.

The three formulations with the least change at all three concentrations used were gum rosin beta-propiolactone adduct reacted with diethylene glycol, maleic-modified adduct, and hydrogenated maleic-modified pine gum. The range for the percent deformation of these formulations was from 71.2 to 116.9.

The formulations using disproportionated rosin reacted with propylene oxide, hydrogenated fumaric-modified pine gum, and the ethylene glycol ester of rosin modified with fumaric acid at all three concentrations became more elastic after aging. The range of percent deformation for the formulations using these rosin derivatives was 110.6 to 233.9.

Mastics using natural rubber – In a natural rubber-based mastic, three formulations had only slight embrittlement, none were more elastic after aging, and seven were noticeably more brittle, as was the gum rosin formulation. Those that exhibited only slight embrittlement were the diepoxides from photosensitized, oxidized pine gum, oxonated gum rosin, and formaldehyde-modified rosin. These ranged from 66.7 to 92.9 percent deformation.

Mastics using styrene-butadiene rubber – In an SBR-based mastic, three formulations had only slight embrittlement and four were more elastic due to aging. Those that exhibited only slight embrittlement contained the pentaerythritol ester of pot residue, zinc salt of pot residue, and hydrogenated fumaric-modified pine gum. A commercial SBR-type mastic also had only slight embrittlement.

In general, none of the formulations being discussed exhibit the elasticity that some of the reclaimed rubber formulations had. Except for two or three values, these could be considered quite good. The four rosin derivatives that cause the mastic to become more elastic are the formaldehyde-modified

rosin, oxonated gum rosin, the pentaerythritol ester of oxonated rosin, and the ethylene glycol ester of fumaric-modified rosin.

Resistance to a Static Load at an Elevated Temperature

The time to obtain failure of a lap joint of 1-square-inch area with a load of 500 grams at 160° F was recorded as the resistance to a static load at an elevated temperature. Eight of the 19 rosin derivatives evaluated in a reclaimed rubber-based mastic passed the test by holding over 24 hours in formulations that incorporated the rosin derivative at three concentrations. Those that passed in the reclaimed rubber-based mastic were the diepoxides from photosensitized oxidized pine gum, formaldehyde-modified rosin, the glycerol ester of fumaric-modified rosin, the residue from the distillation of gum rosin, the pentaerythritol ester of the pot residue, the zinc, salt of the pot residue, hydrogenated maleic-modified pine gum, and hydrogenated fumaric-modified pine gum.

In a natural rubber-based mastic, 12 of the 14 rosin derivatives evaluated had one or more concentrations of derivative in formulations passed the 24-hour test. Of the 14 rosin derivatives, six passed the test at all concentrations. These were the diepoxides from photosensitized, oxidized pine gum, the glycerol ester of fumaric-modified rosin, the pentaerythritol ester of oxonated gum rosin, hydrogenated maleic-modified pine gum, and hydrogenated fumaric-modified pine gum.

In an SBR-based mastic, nine of the 16 rosin derivatives evaluated passed the 24-hour test at all concentrations. Three others had one or two concentrations pass. The rosin derivatives used in this type of mastic that passed the test include the glycerol ester of fumaric-modified rosin, the pentaerythritol ester of oxonated rosin, hydrogenated maleic-modified pine gum, hydrogenated fumaric-modified pine gum, the pentaerythritol ester of the pot residue, the zinc salt of the pot residue, the zinc resinate of formaldehyde-modified rosin, and rosin anhydride. Even though the gum-rosin control and a second commercial SBR-type mastic did not pass on all samples, they did not by any means fail in a few minutes. Here, as in the natural rubber-based mastics, there was no pattern as to failure. The formulation of higher concentrations did not necessarily fail more rapidly than the low-concentration formulation of those mastics that did fail.

The reasons for failure on this type of test are probably many. Three reasons seem to show up from the test results and from data on the preparation of the mastics. These are that failure can to some extent be attributed to (1) the softening point of rosin derivative, (2) compatibility of the rosin derivative with the other ingredients of the formulation, and (3) the effect of the rosin derivative in embrittling or plasticizing the mastic during the test. Four rosin derivatives passed the test in each type of mastic. They are the glycerol ester of fumaric-modified rosin, the residue from the distillation of gum rosin, the hydrogenated maleic-modified pine gum, and the hydrogenated fumaric-modified pine gum. The data can be found in table 3.

Table 3.–Resistance to static load at elevated temperature[1] (500 gram load at 160° F.)

Specimen	Time to failure
	Hours
Residue in reclaim mastic	>24
Zn resinate in reclaim mastic	7/24
Zn salt in reclaim mastic	>24
Penterythritol in reclaim mastic	>24
Zn resinate in natural rubber mastic	~13
Zn resinate in SBR mastic	>24
Commercial mastic A	~24
Commercial mastic B	>24

[1] For phr of derivative corresponding to maximum unaged lap-shear strength.

On the basis of all the evaluations, the following materials can be recommended for use in mastics. These are listed under the type of rubber for which they are recommended.

Reclaimed Rubber-Based Mastics:

(1) Residue from the distillation of gum rosin
(2) Zinc resinate of formaldehyde-modified rosin
(3) Zinc salt of No. 1
(4) Pentaerythritol ester of No. 1

Natural Rubber-Based Mastic:

(1) Zinc resinate of formaldehyde-modified rosin

SBR-Based Mastic:

(1) Zinc resinate of formaldehyde-modified rosin

DISCUSSION

QUESTION: How did you measure the open time?

MR. BUNK: We measured the open time by taking the material and spreading it out on plywood and checking it after certain periods of time. Eventually the material will not adhere to itself. The time right before this was called the open time.

QUESTION: Is it adhesion or cohesion you're measuring?

MR. BUNK: All we're trying to measure is the tackiness, not ad- or cohesion.

QUESTION: Both surfaces were coated?

MR. BUNK: Yes. Both pieces of plywood were coated and we did this by trowelling the material onto the plywood.

MR. BENNETT: This is similar to a tack test in reverse where you would first press the two together, then pull them apart.

QUESTION: Were any measurements made, once they had lost open time, to determine if they could be solvent reactivated?

MR. BENNETT: We did not in this program, but it certainly would be possible. There's an antioxidant in there so no doubt solvent reactivation could restore the tackiness.

POLYGLYCOLS FROM ROSIN

by

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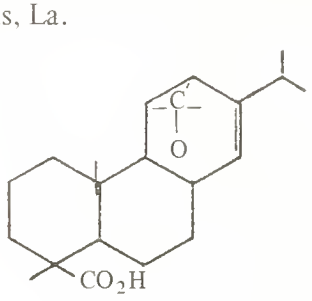
Most industrial uses for rosin are the result of the unique properties of rosin not easily obtainable from synthetic materials. These are gloss, tack (adhesive character), film formation, water repellency, and abrasion resistance. Resin acids in rosin contain one carboxyl group and two double bonds (conjugated in most resin acids), which can be used as a point of attack to make derivatives of rosin. A fairly large number of derivatives have been made, some pure and others quite crude. To keep up the demand for rosin, a continual search for new products and new uses is necessary. The purpose of the present work was to modify rosin by conversion to glycols to enhance its value.

Research at the Naval Stores Research Laboratory, Olustee, Fla., one of the field stations of SURDD, and a number of other laboratories over the past several years have been directed toward making rosin polyfunctional by reaction of selected resin acids and rosin with formaldehyde, dienophiles such as acrylic and fumaric acids, and carbon monoxide.

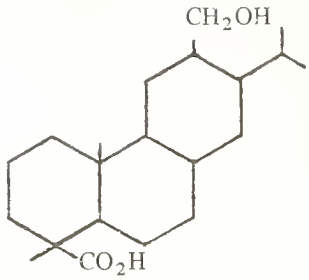
Pure levopimaric acid or the acid in situ in pine gum reacts quantitatively with paraformaldehyde at 100° C. (equation 1) giving the Diels-Alder adduct (I), which is the precursor to other materials (II, III, and IV). Most of this work has been reported. However, recently it has been found that by extraction procedures the adduct can be obtained pure, and if well-developed commercial extraction procedures are used, the cost should be low. The turpentine would not be altered in processing and the residual rosin would be modified but useful as rosin.

PINE GUM
18 TO 25 PCT. LEVOPIMARIC ACID + CH_2O REACTION MIX $\xrightarrow[\text{COUNTER-CURRENT}]{\text{Me OH HEXANE}}$ ADDUCT (I) IN Me OH + TURPENTINE ROSIN IN HEXANE

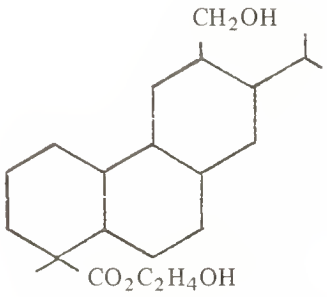
EQUATION 1



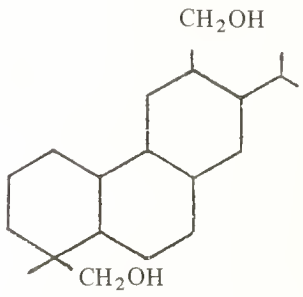
Adduct
I



12-Hydroxymethyltetrahydroabietic Acid
II



Glycol Ester of II
III



12-Hydroxymethyltetrahydroabietand
IV

I believe any of these products could be made available quite cheaply providing large-scale efficient processes were employed for their manufacture. Let us digress a moment and do some speculating.

All of you know the fate of the pine gum industry. The first bit of speculating then will have to be that pine gum will be available preferably at $20.00 a barrel, which from some reports is a possibility.

For the 1968 season, however, the price was $30.00 to $32.00. However, from tests underway using acid paste for stimulating gum flow and plastic lined paper bags to collect the gum, this price should be reduced considerably since the man hours labor will be about one quarter the present figure (4 hours labor per barrel of gum).

Tables 1 and 2, I believe, are significant. The preparation of these chemicals and their disposition must be correlated with the byproduct rosin. Since this byproduct contains less of the abietic type acids than gum rosin, it cannot be sold as gum rosin and must, therefore, be competitive with wood and tall oil rosins.

Item	Lower Limits	Upper limits
Pine gum[1]	$20.00 per bbl.	$30.00 per bbl.
"Levo" cost[1]	$0.05 per lb.; $4.25	$0.077 per lb.; $6.54
Credit for 10 ½ gallons of turpentine	$8.40	$8.40
Byproduct rosin[2]	230 lb.	230 lb.
Cost of gum less credits	$20.00-$12.65 or $7.35	$40.00-$14.94 or $15.06
Materials cost of residual rosin[3]	$0.032 per lb.	$0.065 per lb.

[1] Pine gum 435 lb. net: 10.5 gal.; 74.5 lb. turpentine; 314 lb. rosin; average levopimaric acid ("levo") content 85 lb.
[2] 315 lb. less 85 lb. "levo."
[3] This is no longer gum rosin and must be priced to compete with tall oil or wood rosin.

Table 2.–Some cost estimates on adduct (I)

	Lower limit of cost per lb. of (I)	Upper limit of cost per lb. of (I)
"Levo"	$0.045	$0.070
Paraformaldehyde	.020	.020
Materials	.065	.090
Manufacturing and investment costs (+31 pct.)[1]	.020	.028
Total manufacturing cost	.085	.118
Mark-up 60 pct.[1]	.136	.189

[1] Methods of estimating the approximate manufacturing cost of a chemical product. J.H. Bruun, Program Planning Evaluation (PPE) Staff, ARS, USDA, Sept. 1962.

The materials cost of this rosin with gum at $30.00 a barrel is 6.5¢, which is probably too high to be competitive over the years, especially if the price of turpentine decreases appreciably from the current 80¢ a gallon.

The estimated price of the adduct (I), table 2, are probably at the upper limit of acceptability for the consuming industry except for specialty products. Accordingly, all possible steps will have to be taken to reduce manufacturing costs by using large scale, continuous processes to minimize material losses and labor charges.

These are new materials that could support a new industry and would not necessarily displace rosin used in some other manner. Work described later indicates the usefulness of some of these compounds in polyurethanes, a type of polymer that is particularly attractive. Certainly other uses can be developed. As stated, this could be a new industry; and as it develops, other advantages will surely be apparent.

Products II and IV, if available at the right price, should find many uses, specifically in condensation polymers, polyesters, polycarbonates, polyurethanes, and polyamides. The acid (II) surely could be converted to a dimer and when II polymerizes it gives a high melting colorless resin (m.p. 240° C.). As shown later, it has been converted to an amino acid and diamine. The glycol (IV), likewise, appears to be an extremely attractive compound. We have not had the time to explore all the possibilities and have concentrated on evaluating some of these in polyurethane elastomers, which we will be testing soon in foams. Of course, in polyurethanes, you will know there are an extremely large number of different glycols and diisocyanates available commercially. Accordingly, it has not been possible to consider only a very few of the formulations for polymer preparations.

More or less standard commercial formulations have been published for elastomeric polyurethane films involving the use of polypropylene glycol with toluene diisocyanate (T.D.I.) and hydroxyl-terminated polyethylene glycol adipates with 4,4' diphenylmethane diisocyanate (M.D.I.). The objective in present research was to determine the effect the resinyl moiety had on the polymer properties and to do this it was decided to introduce the rosin molecule

into the polypropylene glycol and the polyethylene glycol adipate chains and react these with T.D.I. Some physical properties of polymers made from glycols varied in this manner are given in tables 3 to 9 inclusive. Until complete results are published we have provided a summary report here.

Table 3. – Monoglycol ester III

$(HOCH_2RCO_2\overset{CH_3}{\overset{|}{C}}HCH_2OH)$; OHE 205

Rosin moiety (P) pct.	Poly mix[1] hydroxyl equiv.	NCO-OH ratio equiv.	Tensile strength p.s.i.	Modulus Elastic	Modulus 100 pct.	Elongation pct.	Stiffness T_f°C	Hardness
0	214	1.05/1	1200	--	567	288	--	--
5.0	212	1.05/1	1678	--	865	277	--	--
10.0	212	1.05/1	5317	13000	1290	251	-16.5	41
14.4	213	1.05/1	5050	49700	1985	220	3.0	63
20.0	212	1.05/1	4716	133000	[2]	170	7.5	79
20.0	[3]308	1.22/1	3794	39000	1524	240	-21	79

[1] Combination of trimethylolpropane, 1.4 – Butanediol, polypropylene glycol 1000, and rosin glycol.
[2] Too hard.
[3] Polypropylene glycol 2000, trimethylol propane, and rosin glycol.

Table 4. – Polyglycol ester-ether

$[H(OCH_2\overset{CH_3}{\overset{|}{C}}H)_xOCH_2RCO_2(\overset{CH_3}{\overset{|}{C}}HCH_2O)_xH]$; OHE 500

Rosin moiety (P) pct.	Polyol mix[1] hydroxyl equiv.	NCO-OH ratio equiv.	Tensile strength p.s.i.	Modulus Elastic	Modulus 100 pct.	Elongation pct.	Stiffness T_f°C	Hardness
0	214	1.05/1	1200	--	567	288	--	--
5.0	212	1.05/1	1680	--	865	277	--	--
10.5	213	1.05/1	5166	8000	780	280	-13	[2]
15.0	213	1.05/1	4750	100000	[3]	253	2.5	73
20.0	213	1.05/1	5270	160000	[3]	194	6.0	86

[1] Combination of trimethylolpropane, 1,4-Butanediol, polypropylene glycol 1000, and rosin glycol.
[2] Too soft.
[3] Too hard.

Table 5. – Polyglycol ether

$[H(OCH_2\overset{CH_3}{\overset{|}{C}}H)_xOCH_2RCH_2O(CH_2\overset{CH_3}{\overset{|}{C}}HO)_xH]'$ OHE 450

Rosin moiety (R) pct.	Polyol mix[1] hydroxyl equiv.	NCO-OH ratio equiv.	Tensile strength p.s.i.	Modulus Elastic	Modulus 100 pct.	Elongation pct.	Stiffness T_f°C	Hardness
0	214	1.05/1	1200	--	567	288	--	--
10	212	1.05/1	2561	2540	436	275	-14.5	48
15	213	1.05/1	4911	9097	694	301	- 1.0	--
22	213	1.05/1	5094	47000	1747	244	5.0	59
24	274	1.05/1	2866	2429	393	347	-50	[2]

[1] Combination of trimethylolpropane, 1.4-Butanediol, polypropylene glycol 1000, and rosin glycol.
[2] Soft.

Table 6. – Comparison of three types glycols

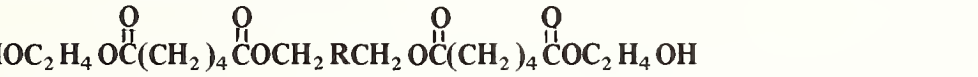
Rosin moiety (P) pct.	Polyol mix hydroxyl equiv.	NCO-OH ratio equiv.	Tensile strength p.s.i.	Modulus Elastic	Modulus 100 pct.	Elongation pct.	Stiffness T_f °C	Hardness
				Monoglycol				
15	213	1.05/1	5050	49700	1985	220	3.0	63
20	212	1.05/1	4716	133000	[1]	170	7.5	79
				Polyglycol ester-ether				
15	213	1.05/1	4750	100000	[1]	253	2.5	73
20	213	1.05/1	5270	160000	[1]	194	6.0	86
				Polyglycol ether				
15	213	1.05/1	4911	9097	694	301	-1.0	--
22	213	1.05/1	5094	47000	1747	244	5.0	59

[1] Too hard.

Table 7. – Comparison of glycol mixtures having varying average molecular weights

Rosin moiety (R) pct.	Average hydroxyl equiv.	NCO-OH ratio equiv.	NCO equiv.	Tensile strength p.s.i.	Modulus 100 pct. elongation	Elongation pct.	NCO reduction pct.
0	214	1.05/1	0.14	1200	567	287	---
0	245	1.2/1	.16	2850	4026	188	---
				Polyglycol ester-ether			
10	213	1.05/1	.14	2946	2545	310	---
19	376	1.07/1	.10	2560	736	310	28
28	307	1/1	.11	2970	12000	325	27
				Polyglycol ether			
10	213	1.05/1	.14	2561	436	276	---
24	274	1.05/1	.117	2866	393	347	16
25	276	1.05/1	.117	2741	312	305	16
28	289	1.09/1	.126	3150	2170	210	10

Table 8. – Polyglycol adipates



Hydroxyl equivalent 343

Rosin moiety (R) pct.	Average[1] hydroxyl equiv.	NCO-OH ratio equiv.	Tensile strength p.s.i.	Modulus 100 pct.	Elongation pct.
--	--	--	[2] 5800	[3] 1300 300 pct.	[2] 500
5	252	1.05/1	2820	125	864
10	252	1.05/1	5905	[4] 368	880
15	252	1.05/1	7111	694	570
20	252	1.05/1	8350	1770	480
25	252	1.05/1	7713	[5]	376

[1] Combination of 1.4 – Butanediol, polyethylene glycol adipate OHE 1000, and rosin glycol.
[2] Commercial sample.
[3] Commercial sample at 300 percent.
[4] 1031 at 300 percent.
[5] Hard.

Table 9. – Polyglycol adipates

Variation in molecular weight

Rosin moiety (R) pct.	Average[1] hydroxyl equiv.	NCO-OH ratio equiv.	Tensile strength p.s.i.	Modulus 100 pct.	Elongation pct.	NCO reduction pct.
20	252	1.05/1	8350	1770	480	---
25	452	1.05/1	3603	343	600	55
30	440	1.05/1	6600	1131	475	57

[1] Combination of 1.4 – Butanediol, polyethylene glycol adipate (OHE 1000), and rosin glycol.

Introduction of either of the rosin moieties II or IV into a polypropylene glycol chain increases the tensile strength up to about 5,000 p.s.i. with rather marked increases in stiffness (modulus) and moderate decreases in elongation.

Of the three types of rosin derivatives tested, the glycol (IV) generally gave the best polymers. There seems to be a correlation between average molecular weight of the glycol and rosin content of the polymer, which results in a considerable reduction in the amount of isocyanates required for polymer formulations (tables 3 to 7).

The same general conclusions were observed with the polyglycol adipates. Extremely good polymers were prepared with as much as 50-percent reduction in isocyanates requirements. The effect of this reduction in cost of the polymer could be pronounced since the isocyanates used commercially in this type polymer sell from 80¢ to $3.50 a pound.

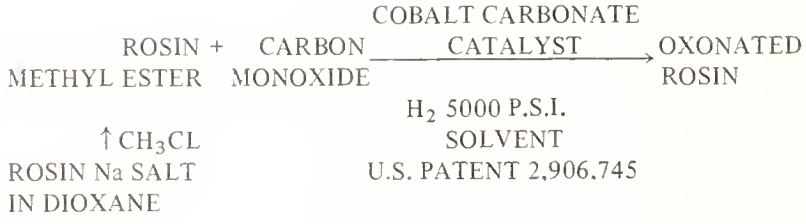
The above deals with plastic films that are important as protective coatings, floor coverings, injection moldings, and elastomers that have a number of uses that can be met by high-grade expensive plastics. The above rosin derivatives should find use in flexible and rigid polyurethane foams – the largest and most important use for polyurethanes.

In 1967, Mobay Chemical Co. published their results on the evaluation of the glycol ester of an hydroxylated rosin derivative, "Vinsol," in rigid foams. The effect of the rigid rosin moiety in the foams was pronounced since stronger foams were obtained that were less flammable, requiring less fire-retardant chemicals and a reduction of 20 percent in isocyanate requirements. The result amounted to a reduction in cost of about 20 percent.

Many of the products we are talking about today certainly can find a use in polyurethane foams. The hydroxy acid (II) and the glycols (III) and (IV) are most important examples under investigation now.

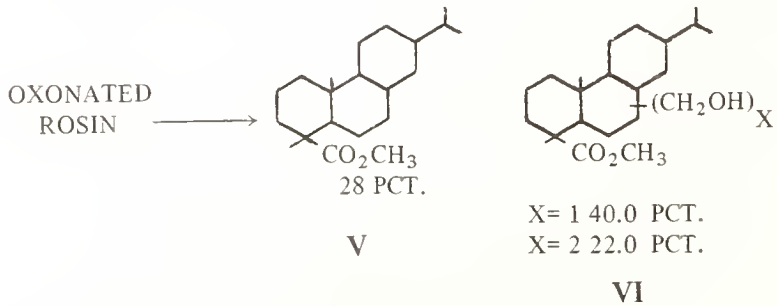
In looking for cheap rosin glycols, in addition to the above, four other preparations have been considered.

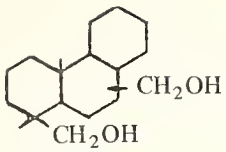
The oxonation of rosin (reaction of rosin and carbon monoxide) has been reported. We, at the Naval Stores Laboratory, have studied this reaction and made some improvements. By using the methyl ester of gum rosin (Equation 2) instead of the free acid, a substantial increase in yield (20 percent) was obtained. The ester lessened the problems associated with removal of catalyst, eliminated inter-ester formation, and resulted in an efficient separation of products by countercurrent extraction by partitioning between 95 percent aqueous methanol and hexane. The methyl ester was also particularly useful



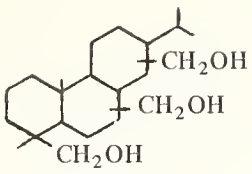
Equation 2

for the copper-chromite conversion of the carboxyl function to a methylol group. The products of the reaction are shown in V through VIII inclusive. In this group the rosin derivatives are completely hydrogenated and if available commercially should have a considerable impact on the rosin market.



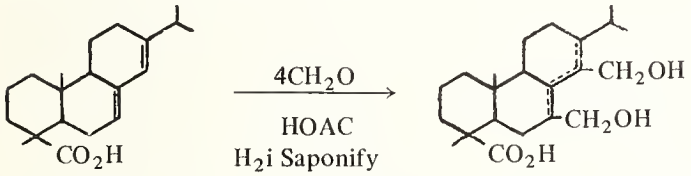


DIOL
VII



TRIOL
VIII

The products from the reaction of rosin and formaldehyde in acetic acid resemble the products from the oxonation of rosin. Recent work on the reaction of abietic acid (IX) with formaldehyde in acetic acid has resulted in the preparation of 7, 14-dihydroxymethylabietic acid, which when hydrogenated gives 7,14-dihydroxymethylhydroabietic acid (X). This can be converted to a triol by reduction of the carboxyl group or reaction of the carboxyl with alkalene oxides.

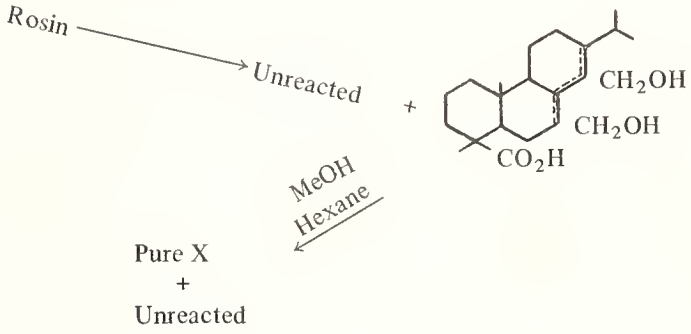


Abietic Acid
IX

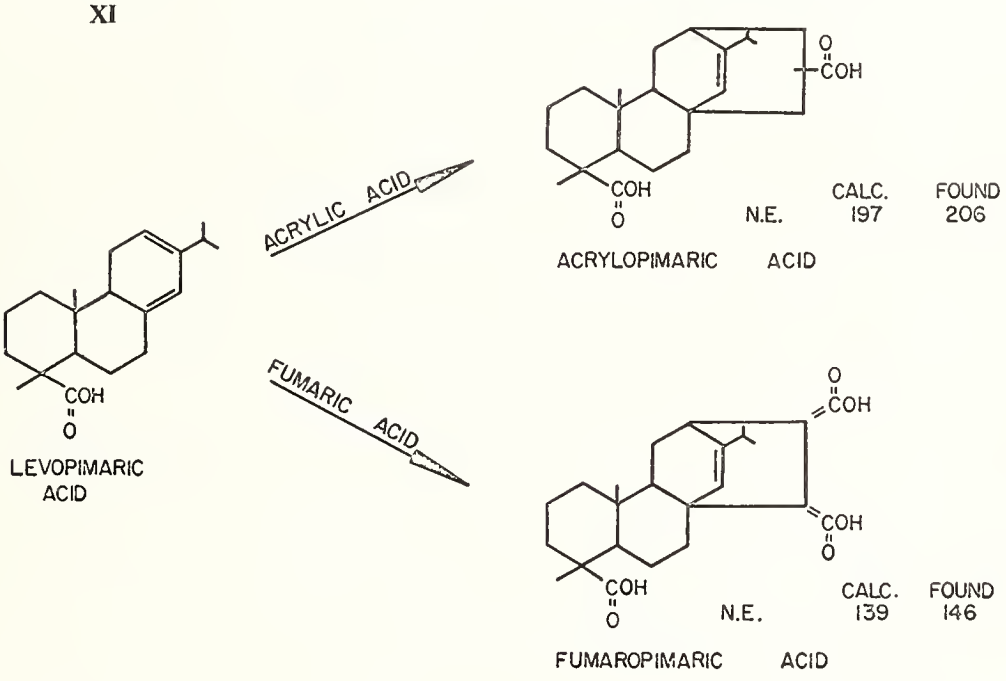
7,14-Dihydroxymethylabietic Acid
80 to 85 pct.
X

Triols
XI

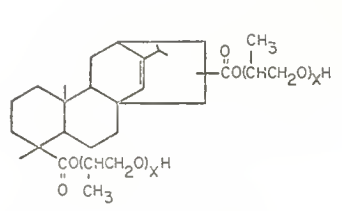
Since about 60 percent of the resin acids in rosin are of the abietic type, the same reaction occurs with rosin. The crude rosin reaction product may be of use in rigid polyurethane foams. Separation of the dihydroxymethyl derivative from rosin has been achieved by countercurrent extraction with the methanol-hexane system mentioned before. Maximum yield of 50 grams of pure diol (X) has been obtained from 100 grams of rosin.



Another route to rosin polyols, which has received some attention has been with the reaction products of levopimaric acid and rosin with acrylic and fumaric acids (equation 3). The reaction of the resulting acids with alkalene oxides is an easy synthesis for another series of polyols, some of which are mixtures (XII through XV inclusive).

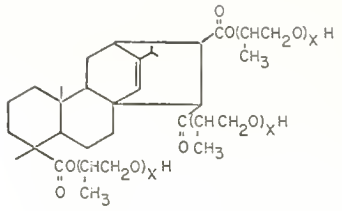


EQUATION 3



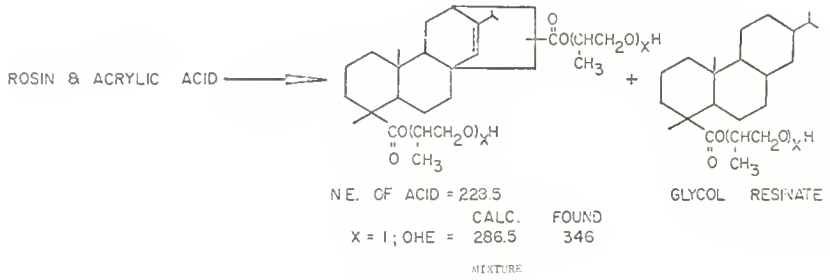
CALC. FOUND
X = 1; OHE = 264 292

XII



CALC. FOUND
X = 1 ; OHE = 197 260

XIII

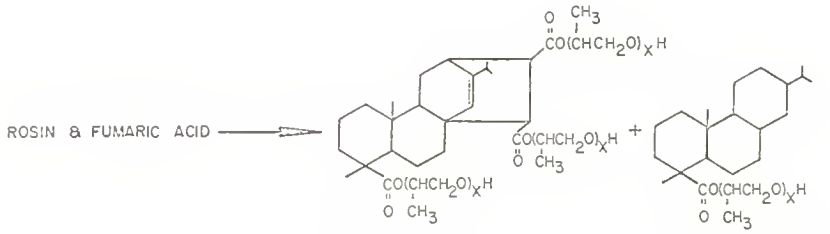


N.E. OF ACID = 223.5
GLYCOL RESINATE

CALC. FOUND
X = 1; OHE = 286.5 346

MIXTURE

XIV

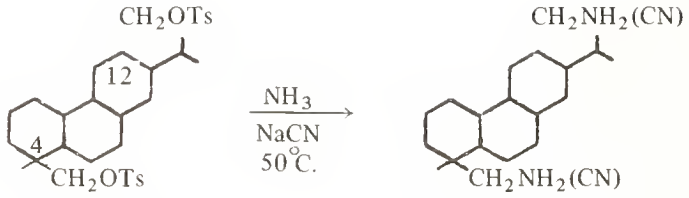


N.E. ACID = 180
GLYCOL RESINATE

CALC. FOUND
X = 1; OHE = 238 381.4

MIXTURE

XV



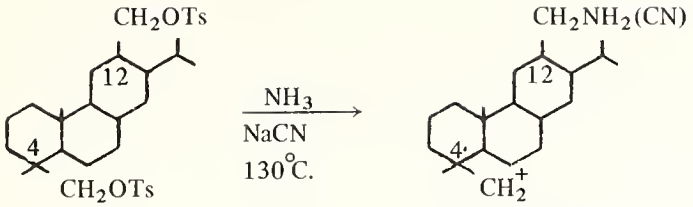
Ditosylate Diamine or Dinitrile

Ts = p-Toluensulfonic Acid Radical

XVI XVII

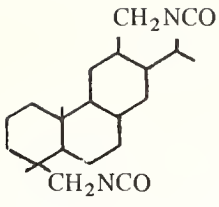
A fairly large number of hydroxymethylated rosin derivatives has been reported. Chemical literature contains descriptions of methods for converting hydroxyl groups to amino and cyano groups. It was obvious then that some of these hydroxy derivatives might be upgraded to more expensive amino alcohols, diamines, dinitriles that can be hydrolyzed to acids, and diisocyanates.

Reactions to prepare rosin diamines and diisocyanate have been explored and the following is a brief description of our work. The glycol IV was converted to the di-p-toluenesulfonic acid ester (tosylate), (XVI), and reacted with ammonia and sodium cyanide in hopes of obtaining XVII. Replacement of the tosylate on the C_{12} hydroxymethyl was quantitative. Partial replacement on the C_4 carbon was obtained at about 50°C. but above this temperature tosyl elimination at the C_4 carbon started (XVIII) and at higher temperatures (130° C.) was the only reaction. Studies have not been completed on this phase, however, since the reaction is solvent-temperature dependent, success may not be far away. The diamine was



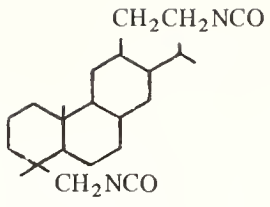
Tosly Elimination

XVI **XVIII**



Diisocyanate

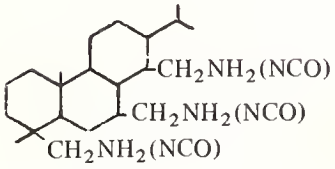
XXI



Diisocyanate

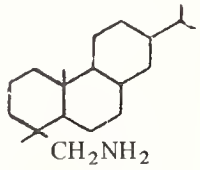
XXII

prepared by conversion of the amide XIX via hydrogenation, and the two amines XX were converted to diisocyanates by reaction with phosgene at about 170° C. (XXI and XXII). Pure compounds were used in the original investigations. The reactions, however, are general and the information learned can be applied to less pure derivatives to prepare, for example XXIII and XXIV from rosin.



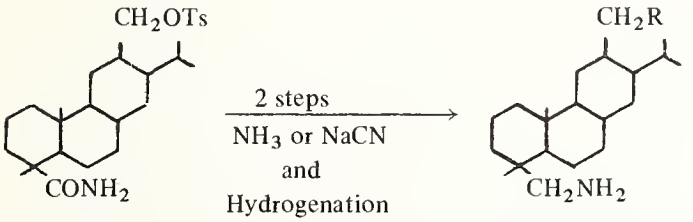
Triamine
Triisocyanate

XXIII



Rosin Amine
Distilled from
Triamine

XXIV



Amide

R = $-NH_2$ or $-CH_2NH_2$

XIX **XX**

In summary, this report describes some interesting rosin derivatives that may find many uses by the chemical industry. If there are any questions, I will try to answer them. I have enjoyed talking to you and hope you have found the contents of this presentation interesting and of value.

QUESTION: What was the catalyst used in the alkylene oxide reaction?

DR. HEDRICK: DMF was used as solvent for monoadditions. These are high melting materials, and we have to dissolve them in something, otherwise you can't get them to react. Where more than one mole is added, KOH is the catalyst. Unless you have solvent in there, the melting points you're talking about are 190° to 200° C. Now, if we had a situation where we had a molten material, it would be fairly simple. You'd add in the right amount of alkylene oxide and have no trouble. But if we put in the solvent, melt it, and then add the alkylene oxide, it would blow up. We had to add the solvent to lower the flux.

QUESTION: Do you feel the residual catalyst in the product will have any effect in the reaction with isocyanate?

DR. HEDRICK: We give each sample an acid wash, a good acid wash, to remove any catalyst.

COMMENT: Then if a molten reaction medium instead of solvent were used you would still have to dissolve the product in solvent to remove the catalyst. You recommend removal of catalyst.

DR. HEDRICK: For polyurethane, yes. I don't know what the commercial practice is today for polyurethane. How they get the catalyst out I don't know.

QUESTION: How do you react the glycol with the isocyanate? Under what conditions? At what temperature?

DR. HEDRICK: We mix the glycol and isocyanate and heat to 70° C., then pour it on a plate and cure.

QUESTION: Is it instantaneous?

DR. HEDRICK: No.

QUESTION: Do you use a catalyst such as tin compounds at this stage?

DR. HEDRICK: No. We can't get a small enough amount of tin. Even the smallest amounts tried cause the mixture to gel almost immediately. In our research we are working with 500 g. of material. On a large scale where you're talking about a pound of catalyst per thousand pounds of material or something like that you can.

COMMENT: We use tin and keep diluting until we get a usable concentration.

DR. HEDRICK: We can't use tin. It makes our reaction go too fast.

QUESTION: In this work the viscosity of components is very important since you have to pump them. What are the viscosities of your polyols and isocyanates?

DR. HEDRICK: They're quite high. You'd have to dilute them. I don't know whether you're familiar with the work Mobay published in this area or not.

COMMENT: That was one of the problems Mobay had.

DR. HEDRICK: I can understand that. But, at least, according to the article they were able to handle it in the foaming machine.

COMMENT: You can always to it in small scale equipment.

DR. HEDRICK: These are quite viscous materials, and you'd expect that they'd lump in the middle of the run.

COMMENT: If I recall the Mobay work right they used a 20-to-30-percent material.

DR. HEDRICK: Mobay used as high as 50 percent. In that publication the presence of rosin derivatives in the foam reduces the cost 20 percent. You can use a higher molecular glycol. The average molecular weight is higher. The rosin molecule is more rigid, which permits the use of less isocyanate to get the rigidity that you have to have. The product is less flammable. Because of this the content of phosphorus compounds may be reduced as much as 20 percent. The overall cost reduction is 20 percent.

QUESTION: Do you realize that the prices of polyurethane polyols has come down considerably in the last few years?

DR. HEDRICK: We did not set out to make the best polymer. This is our next step. We tried to find out what effect the rosin molecule had on these particular polymers. We have data to show that the expected effect in modulus is there. In fact, it is a lot more elastic than I expected it to be. If we can reduce the isocyanate by 50 percent we will have a good market. We feel we have some interesting polymers. We have discussed them with about 20 chemical companies and they appear quite interested. If someone would offer samples I'm sure there would be quite a market.

QUESTION: Are these materials clear? What happens on exposure to weather and UV?

DR. HEDRICK: The diisocyanate we used (tolylene diisocyanate) is not stable to light.

QUESTION: Have you considered any of the aliphatic isocyanates? At $2.00 a pound?

DR. HEDRICK: We have looked at them briefly but have no data to report at this time. It is difficult to look at many compounds because we must make our own starting materials in most cases. We have made up to 30 pounds of copper-chromite in our pilot plant, which makes it fairly practical, but our other equipment for this purpose handles only small amounts.

ROSIN DIMERS–PROGRESS REPORT

by

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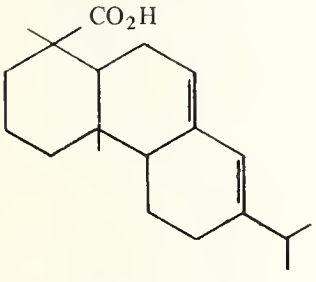
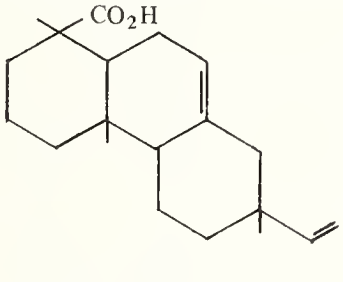
The use of resin-acid dimers has been important in the adhesives industry for a number of years. The main objective of our present research is to improve the dimerization reaction, hopefully to obtain good yields of pure resin-acid dimers. Improvements in the dimerization reaction should improve the potential of existing markets for rosin materials. Resin-acid dimer products are enjoying a good market. An improved synthesis might also stimulate new uses of gum rosin and derivatives. For example, high-purity resin-acid dimers could be useful in condensation-type polymerizations. The dicarboxylic dimer would represent a comonomer for preparation of novel polyesters and polyamides, etc.

The dimerization of rosin-related materials has been the subject of the patent literature for nearly 40 years, however, for the conventional uses of dimerized rosin, very little characterization of the reaction was found necessary. Thus, acid number, softening point by the ball and ring method, and color account for most of the evaluation of dimerizations that have been reported. Two reports by French authors, one by Brus and one by Morrillon, describe some tedious isolation procedures resulting in less than 10-percent yields of dimers from crude products[1]. The intent of the present research is to optimize the dimerization by careful study of individual reaction factors.



Abietic Acid



Isopimaric Acid

Abietic acid, isopimaric acid, and gum rosins were dimerized. It was felt that dimerization of pure abietic acid, one of the principal components of gum rosin, would provide a simpler chemical model than gum rosin itself. A typical gum rosin analysis shows that this starting material contains approximately 7 percent neutral compounds, 8 percent dehydroabietic acid, 20 percent isopimaric acid with sizable percentages of the remainder being of the abietic type resin acid.

In a typical experiment, pure abietic acid was mixed under selected conditions with acid catalyst. Crude products, freed of catalysts by extraction, were analyzed by either gel permeation (GPC) or gas chromatography (GC). These analyses provided relative estimates of dimeric and monomeric size species without regard to acid functionality.

The data of table 1 show some typical analyses by

Table 1. –Comparisons of analyses of crude dimerization products of resin acids.

Sample	Weigh percent dimer By GPC	By GC
26032-79	9	10
26032-84	<1	0
26032-86	22	18
26032-87	39	38
26032-88	65	75
26032-89	65	73
26032-90	83	79
26032-92	29	29
26419-25	85	77
26419-31	79	83
26419-40	84	81
26419-44	70	69
26419-45	71	76
26419-47	75	82
26419-54	77	75
26419-55	80	74
26419-63	82	81
26419-64	61	64
26419-65	87	81
26419-68	91	80
26419-71	68	65

[1] Bardyshev, I. I., and Strizhakov. Dok. Akad. Nauk.SSSR, 181:343. 1968.Morrillon, Yves. Double Liason 105: 41. 1964. Morrillon, Yves. Double Liason 106: 91. 1964. Brus, G. Le-Van-Thoi, M"eh. Francois. Peintures, Pigments, Vernis, 29: 36. 1953.

both methods. The independent methods agree with each other by +5 percent at low, intermediate, and high dimer levels in crude dimerization products. GPC, which analyzes by size, has the advantage of operating at lower temperature, 23° C. Possible thermal changes in the sample are avoided. Very high or low boiling components that might be overlooked by GC are observed by GPC. The GC method has the advantage of better resolution for a given analysis time. Analysis by GC is performed on the methyl esters. The methylated dimer components elute in the vicinity of 330° C.

By rapid determination of the results of a given dimerization, more than 200 dimerizations were performed on abietic acid to single out individual reaction parameters. Once it was felt that the dimerization conditions had been optimized, other starting materials such as gum rosin were employed.

The most important influences on the course of the dimerization of abietic acid were found to be choice of catalyst, acid strength of the catalyst, ratio of the amounts of abietic acid and catalyst, and the solvent employed for the reaction.

Figure 1 shows a plot of some data where the amount of 89 percent sulfuric acid varied. Reaction time, temperature, and other variables were held constant. A point was reached at a molar 2:1 ratio of sulfuric to abietic acids where a sharp increase in dimer yield was obtained. Further increase in the amount of catalyst lowered the acid percentages without significantly increasing the yield. The percentage neutrals (100 percent acid) was representative of the loss of acid functionality and the amount of side reactions that occurred. The two curves have approximately the same shape.

The data of figure 2 show the influence of acid strength on the dimerization reaction. Again, other

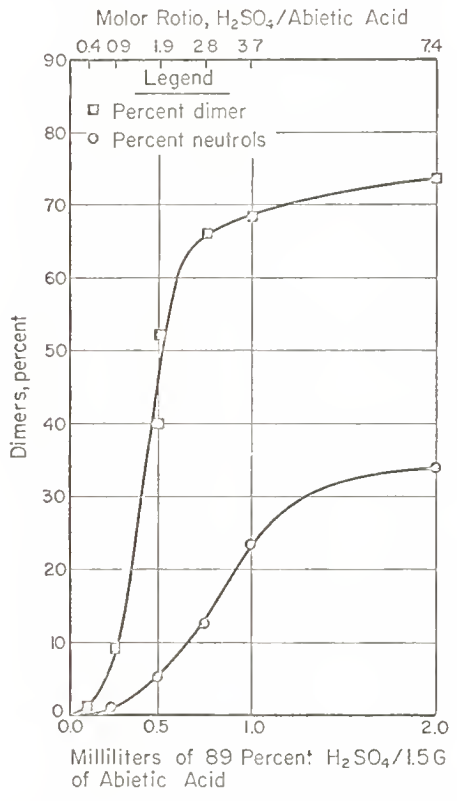


Figure 1.—Yield of resin-acid dimers and byproduct versus concentration of sulfuric acid used in dimerization.

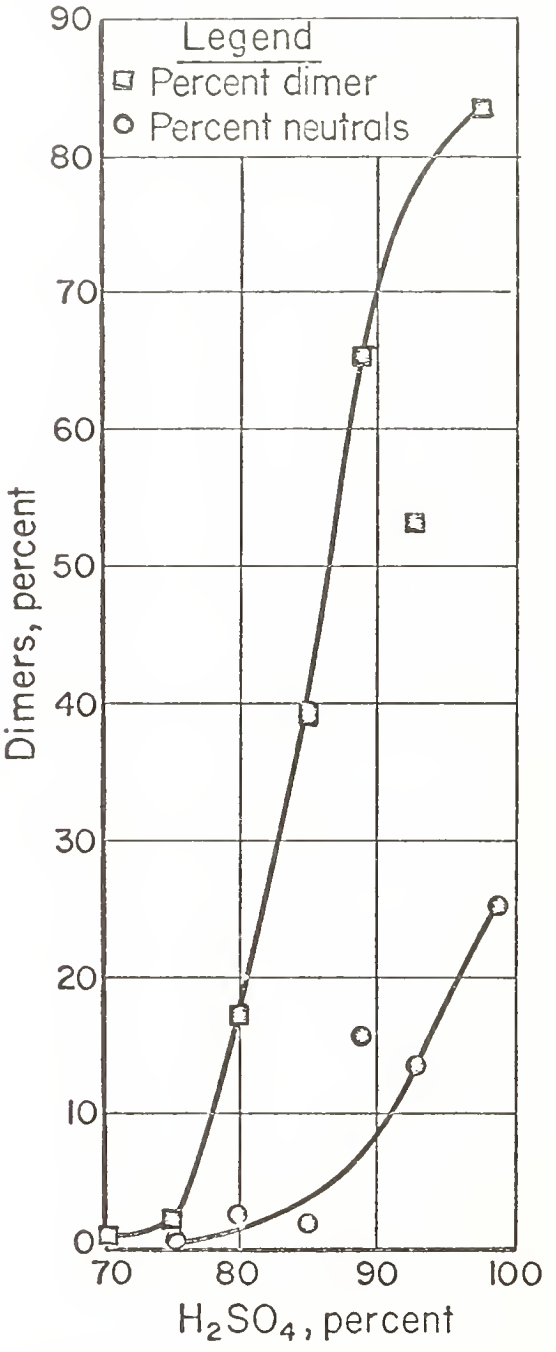


Figure 2.—Yield of resin-acid dimers and byproduct versus the acid strength of sulfuric acid used in dimerization.

reaction influences were held constant. The dimer yield increased sharply with acid strength. Neutral compound formation is similar to the previous figure, showing parallel behavior to dimer formation. The main reaction and the side reaction appear to proceed at proportional rates. This point will be returned to later, but it has been observed that side reactions limit the dimer yield to 80 percent dimers. The side reaction that predominates is primarily the well-known disproportionation reaction.

The data of figure 3 show a plot of variable amount of concentrated sulfuric acid as catalyst. As compared to the previous figure showing data for 89 percent sulfuric acid, this curve shows a narrow maximum in the dimer yield in the vicinity of a 2:1 molar ratio of catalyst to abietic acid. It can be seen that concentrated sulfuric acid (a frequently used catalyst by industry for rosin dimerization) must be measured carefully against the amount of rosin material for best results.

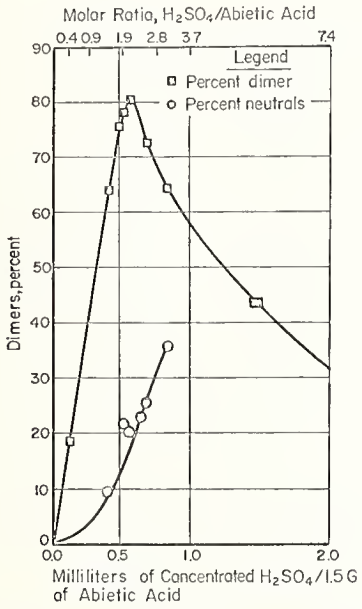

Molar Ratio, H_2SO_4/Abietic Acid
0.4 0.9 1.9 2.8 3.7 7.4
Legend
Percent dimer
Percent neutrals
Dimers, percent
0 10 20 30 40 50 60 70 80 90
0.0 0.5 1.0 2.0
Milliliters of Concentrated H_2SO_4/1.5 G of Abietic Acid

Figure 3.—Yield of resin-acid dimers and byproduct versus concentration of sulfuric acid used in dimerization (from data of table 2).

Given below is a very general chemical kinetic scheme. Abietic acid (AA) becomes protonated in a

$$(AA) + (H^+) \underset{\text{FAST}}{\overset{\text{FAST}}{\rightleftharpoons}} (AA{-}H^+) \xrightarrow[(AA)]{\text{SLOW}} (AA{-}AA^+) \xrightarrow[-H-]{\text{FAST}} (\text{DIMER}$$

$$\text{RATE} = k(AA)\,(AA{-}H^+)$$

fast reversible step, followed by a slow step as the first step in dimerization. Thereafter, fast proton and double-bond shifts lead to isomeric dimer species. This scheme is generally consistent with the experimental results in which the rate is dependent on both the amount of sulfuric acid and abietic acid.

The data of table 2 show some results demonstrating the influence of solvent on the dimer yields.

Table 2.—Yield of dimers of abietic acid using different solvents during reaction

Solvent	Reaction time, hr.	H_2SO_4 percent	H_2SO_4 ml[1]	Temperature, °C., ±3	Reaction product percent		
					Dimer	Acid	Material balance
$CHCl_3$	15	89	2.0	25	73	66.1	96
n-Heptane/E+$_2$0, 50/50	15	89	2.0	25	10	98.2	97
Toluene	4	89	2.0	25	57	51.7	97
Toluene	4	89	.50	25	48	86.5	102
$CHCl_3$	5	89	.62	25	48	95.3	93
E+$_2$0	16	93	.06	25	<1	100.0	100
E+$_2$0	64	93	.60	25	9	96.0	104
$CHCl_3$	14	93	.59	25	53	86.8	105
GLYME	15	98	.55	25	<15	104.0	98
GLYME	15	98	.06	25	<7.5	99.2	95
Con. H_2SO_4	5	98	20.0	25	16	83.5	92

[1] Per 1.5g. of abietic acid.

The acid percentages were derived from titration data using the equivalent weight of abietic acid. The material balance reflects the percent of material product received from the basis of abietic acid charged into the reaction. It remains close to 100 percent in all of the data. The best solvent was found to be chloroform. Solvents containing such oxygen functions as ether or glyme lower the acid strength of the catalyst and the yields obtained.

The data of table 3 show some further comparisons of solvent effects at constant, optimum conditions of acid strength, balance of H_2SO_4/AA, etc. Chloroform is again seen to be the best solvent.

Table 3.—Comparisons of hydrocarbon with halogenated compounds as solvents for dimerization reaction

Solvent	Reaction time, hr.	Temperature °C.	Reaction product, percent: Percent dimer GPC	Percent dimer GC	Acid	Material balance
n-Heptane	5.0	44	58	30	61.2	91
$CHCl_3$	5.0	44	61	45	80.9	100
CH_2Cl_2	5.0	35	–	67	70.4	103
$CHCl_3$	5.0	35	82	81	83.9	97
CCl_4	5.0	44	–	58	67.8	106
$CHCl_3$	5.0	44	–	81	80.1	106
90/10 $CHCl_3$/ heptane	5.0	44	–	78	82.0	102
75/25 $CHCl_3$/ heptane	5.0	44	–	79	78.6	102
50/50 $CCHCl_3$/ heptane	5.0	44	–	71	71.5	102
o-Dichloro-benzene	2.0	44	–	56	72.8	–
$CHCl_3$	2.0	44	70	69	83.2	102

Petroleum-type solvents generally derive lower yields and acid percentages and more complex products, which are somewhat blackened and poorly soluble in most solvents. The solvent has easily discernible influences on the dimerization, but the influence is not correlatable with dipole or dielectric strengths. Most of the work now uses chloroform as the preferred solvent.

The data of table 4 show the effect of reaction time on the dimerization reaction at optimized conditions. The reaction is nearly complete in 1 to 2

Table 4. – Effect of reaction time on dimerization reaction

Reaction time, hr.	Temperature, °C	Reaction product, percent: Percent dimer GPC	Percent dimer GC	Acid	Material balance
1.0	44	61	64	86.3	101
2.0	44	70	69	83.2	102
3.5	44	75	82	78.3	103
5.0	44	84	78,83	83.4	102
5.0	44	83,87	77,77	77.3	103
7.0	44	87	81	80.7	104
15.0	44	79	83	79.6	102

hours, and from 2 to 7 hours, little change is noted.

The data of table 5 show some comparisons of different reaction temperatures employed with otherwise optimized reaction conditions. From approximately 25° to 50° C., essentially constant results were obtained. Above 50° C. degradation becomes a problem and below room temperature the rate is noticeably slower. For a given extent of conversion the acid numbers are the same in the approximate range -10° to 50° C.

Table 5. – Comparison of reaction temperatures on dimerization reaction

20 ml. solvent	Temperature, °C	Reaction time, hr.	Reaction product, percent: Percent dimer GPC	Percent dimer GC	Acid	Material balance
$CHCl_3$	-10	22	--	69	90.7	102
$CHCl_3$	0	5.0	55	59	89.3	103
$CHCl_3$	25	5.0	77	--	84.1	102
$CHCl_3$	35	5.0	82	77,84	83.9	97
$CHCl_3$	44	5.0	84	78,83	83.4	102
$CHCl_3$	44	5.0	83,87	77,77	77.3	103
$CHCl_3$	61	5.0	77	--	67.7	80
$CHBr_3$	89	1.0	53	32	<55	118

The data of table 6 reveal the influence of the concentration of abietic acid. The concentration of the chloroform solution of abietic acid, which is in contact with a fixed amount of sulfuric acid, must be altered considerably before large influences are seen in the results. It has also been observed that the optimum ratio of abietic to sulfuric acid changes slightly with the amount of solvent.

Table 6. – Dependence of dimerization on abietic acid concentration

Solvent, Ml.	Temperature, °C	Reaction product, percent: Percent dimer GPC	Percent dimer GC	Acid	Material balance
5	44	72	--	69.7	101
10	44	92,89	80	79.6	100
20	44	83,87	77,77	77.3	103
20	44	84	78,83	83.4	102
40	44	53	--	91.6	102

The data of table 7 show some data obtained under optimized conditions for a number of different

Table 7.–Comparison of dimerization of different rosin-derived materials

Reactant	Reaction time,hr.	Reaction product, percent: Percent dimer GPC	Percent dimer GC	Acid	Material balance
Abietic acid	5.0	83,87	77,77	77.3	103
WW gum rosin	5.0	59	45	80.9	100
WW gum rosin	2.0	59	–	77.0	99
Pine gum	2.0	54	–	64.0	108
Neutrals-free gum rosin	5.0	49	–	82.2	94
Neutrals-free gum rosin	5.0	56	55	78.2	99
Abietic acid	2.0	70	69	83.2	102
50 pct. neutralized gum rosin	5.0	55	–	74.4	100
Isopimaric acid	5.0	31	33	58.6	96
Levopimaric acid	5.0	77	75	80.2	106
Methyl abietate	5.0	80	74	4.3	99
Methylated gum rosin	5.0	67	–	3.4	104
Wood rosin	5.0	–	56	71.2	100
Tall oil rosin	5.0	–	49	72.7	100

starting materials. Abietic acid routinely yields 80 to 90 percent dimers. Gum and wood rosins exhibited approximately 50 to 60 percent dimer yields under the same conditions. However, the acid percentages for wood rosin were lower. Pine gum was nearly as good as the rosins. Tall oil provided slightly lower results. It has been observed that approximately one-third of isopimaric acid will dimerize under the optimum conditions. It is noted that isopimaric acid is a nonconjugated diene, which dimerized somewhat differently than the abietic acid type, resin acid. The respective GC patterns are qualitatively different.

The data of table 8 show some data using aluminum chloride and zinc chloride as catalyst. The amount of catalyst, ratio of $ZnCl_2/AlCl_3$, tempera-

Table 8. – Catalysis by $AlCl_3 - ZnCl_2$

Reactant	Catalyst, g[1]	Reaction time, hr.	Reaction product: Temperature, °C	Percent dimer	Percent acid
Abietic acid	0.48	2.0	25	10	94.4
WW gum rosin	.48	2.0	25	6	89.0
Abietic acid	.48	2.0	25	25	83.5
Abietic acid	.49	2.0	25	15	86.9
Abietic acid	1.5	5.0	35	37	94.0
Neutrals-free gum rosin	1.5	5.0	35	27	81.8
WW gum rosin	1.5	5.0	44	34	75.9
Abietic acid	1.5	5.0	44	9	94.1
50 pct. neutralized gum rosin	2.0	5.0	44	40	84.2
WW gum rosin	10 g	5.0	40	13	--
WW gum rosin	1.5	5.0	44	44	87.3
WW gum rosin	1.5	5.0	44	19	88.0
WW gum rosin	1.5	5.0	44	36	80.0
Isopimaric acid	1.5	5.0	44	19	82.4
WW gum rosin	1.5	1.0	200	35	20.0

[1] Per 1.5 g. of starting material.

ture, and reaction time were varied without obtaining the good yields found with sulfuric acid catalyst. The acid percentages are not as good as the results with H_2SO_4.

The data of table 9 show some data obtained using boron triflouride as catalyst. It has been observed that BF_3 gas or etherate has not been as effective a catalyst as H_2SO_4. Dimer yields and acid percentages are generally lower.

Table 9.–Catalysis by saturated solutions of boron triflouride in chloroform

Starting material	Reaction time, hr.	Temperature, °C.	Reaction product, percent: Percent dimer GPC	Percent dimer GC	Acid	Material balance
Abietic acid	2.0	24	47	33	71.4	100
WW gum rosin	2.0	24-44	61	54	48.7	97
Neutrals-free gum rosin	2.0	25	–	31	69.6	86
Neutrals-free gum rosin	5.0	40	–	19	93.7	100
Neutrals-free gum rosin	5.0	40	–	23	91.0	100
50 pct. neutralized gum rosin	2.0	25	–	33	63.3	90
Methyl abietate	3.0	24-44	–	50	4.6	100

The data of table 10 show some comparisons of a variety of different catalysts. Catalysts such as 85 percent phosphoric acid and 89 percent H_2SO_4 are generally inefficient. Such catalysts as $AlCl_3$, PF_5, and

Table 10.–Use of different catalysts for dimerication of abietic acid under similar conditions

Catalyst: Type	Catalyst: Amount[1]	Reaction time, hr.	Temperature, °C	Reaction product, percent: Percent dimer GPC	Percent dimer GC	Acid	Material balance
Con. H_2SO_4	0.55 ml.	5.0	44	84	81	83.4	102
85 pct. H_3PO_4	0.98 ml.	5.0	44	<2	<2	98.9	99
PF_5	[1]	2.0	25-50	< 5	–	4.0	>100
BF_3	[1]	2.0	24	47	33	71.4	100
89 pct. H_2SO_4	0.62 ml.	2.0	25	29	–	97.2	100
Con. H_2SO_4	0.55 ml.	2.0	25	68	65	85.5	103
$AlCl_3$-$ZnCl_2$	0.48 g.	2.0	25	–	25	83.5	104
Anhy. p toluene sulfonic acid	3.2 gl/50/ml.	40	61	–	38	64.9	100
Anhy. p toluene sulfonic acid	1.94	5.0	44	–	38	98.4	100
101 pct. H_2SO_4	0.55 ml.	2.0	44	71	76	77.8	102
Con. H_2SO_4	0.55 ml.	2.0	44	70	69	83.2	102

[1] Saturated solution.

$ZnCl_2$ are not as efficient as H_2SO_4, and more degraded products are obtained. Concentrated sulfuric acid, 95 to 98 percent, yields results equivalent to that obtained with 101 percent H_2SO_4. Anhydrous p-toluene sulfonic acid has yielded as high as a 85 percent yield of dimers, but the acid percentages are somewhat lower than with H_2SO_4.

The four reactions of figure 4 show a mechanistic scheme accounting for the foregoing empirical observations. According to the proposed mechanism, an

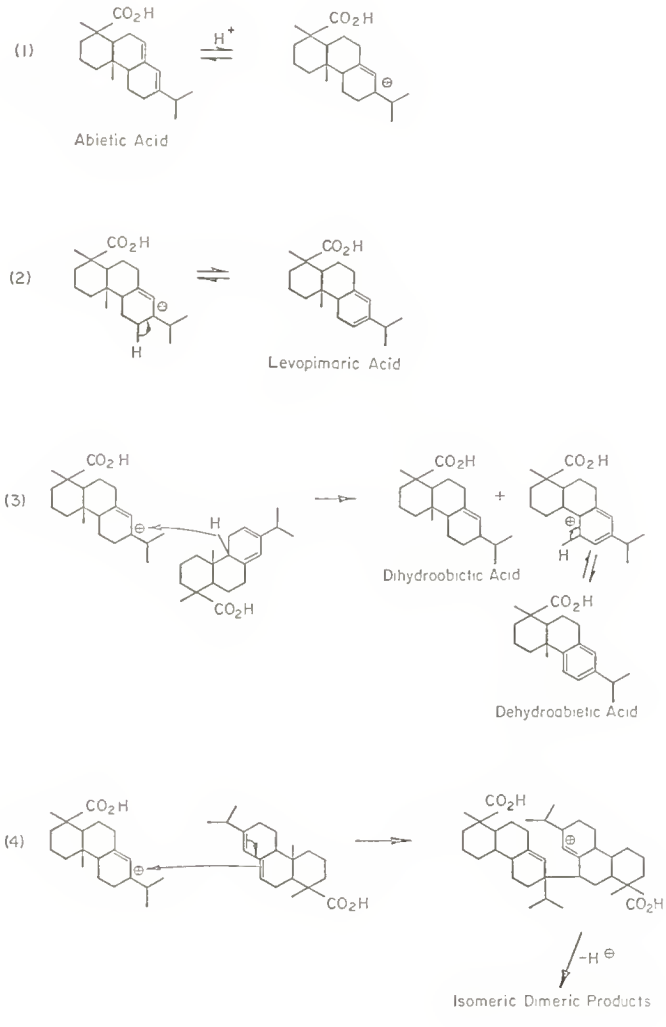


Figure 4.

intermediate carbonium ion can take part in three processes:

(1) Equilibrium with levopimaric (fig. 4, equation 2) or abietic acid (fig. 4, equation 1)

(2) Abstraction of a hydride from levopimaric acid (fig. 4, equation 3) leading eventually to dihydro- and dehydroabietic acids as disproportionation products.

(3) Attack on the diene system of abietic acid as a first step in dimer formation.

The scheme shows two competitive reactions proceeding from a common carbonium ion. The process of equation 4 (fig. 4) leads to dimer formation and that of equation 3 (fig. 4) to by-products. It is not suprising that solvent effects are important to these polar processes. However, the ratio of product to by-product would be difficult to predict since both processes are polar. Experimentally, it has been noted that reaction products are somewhat different when different solvents are used. The respective chromatograms are qualitatively different with regard to both monomeric and dimeric products. It would not be expected that concentration would have significant effect on the ratio of product to by-product since both competitive reactions are bimolecular. This is also consistent with the experimental results. The temperature coefficients for the rates of both reactions conceivably could be quite different. However, the experimental observations show approximately the same ratio of product to by-product over the range -10° to 60°C.

Figure 5 is typical of a GC chromatogram of a dimerization product. On the left some of the components of the monomeric species have been

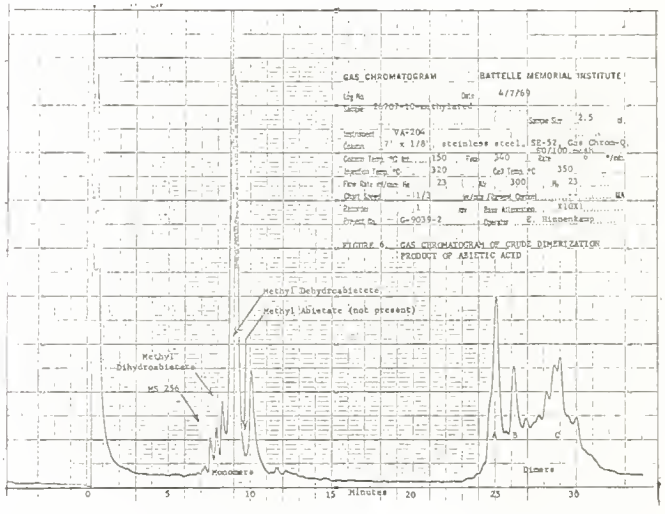


Figure 5.—Gas chromatogram of crude dimerization product of abietic acid.

identified by mass spectrometry and coinjection of sample with authentic standards. The principal by-product has been identified as dehydroabietic acid. Dihydro- and decarboxylated species have also

been observed. The dimer region of the chromatogram has been sampled at several points (A,B, and C) and submitted to analyses by mass spectrometry. The expected value of 632 for the mass to charge ratio has been observed in each case. Thus, the crude products are approximately 80 percent the difunctional resin-acid dimers.

In summary, the yield of resin-acid dimers is limited to 80 to 90 percent by the well-known disproportionation, side reaction. The most important dimerization conditions are choice of catalyst, ratio of H_2SO_4/AA, acid strength of the catalyst, and the employed solvent.

DISCUSSION

QUESTION: Were the percentages listed weight percents or mole percents?

MR. SINCLAIR: Weight percent.

QUESTION: Did you consider the use of suspended clay–acid catalyst systems?

MR. SINCLAIR: No. There are a whole host of catalyst systems possible. We picked three that were often dealt with in the patent literature. We welcome suggestions on a suitable catalyst system. Most of the systems in the literature are in patents, and these are not often detailed enough for ready application.

QUESTION: What are the melting points of your materials and how do they compare to what has been reported?

MR. SINCLAIR: This is mentioned in the patent file. The patent literature lists softening points by the ball and ring method of approximately 80° to 120° C. Our crude products (80 percent dimer–80 percent acid) have a ring and ball softening point of 162°. Some were much higher.

QUESTION: Was there much color change when sulfuric acid concentration was changed?

MR. SINCLAIR: Yes. As a matter of fact in a typical preparation using the better acid catalysts one can get almost every color in the rainbow. In that second figure where the acid strength was varied from 60 to 100 percent, the lower acid strengths resulted in very little reaction, the dimer yield was very low and very little color was observed. As the reaction proceeds to better yields more color is obtained. We have gotten all colors – bright emerald green, yellow, red and purple – during the course of the reaction.

QUESTION: Will you elaborate on your method to remove neutrals? How complete was this removal?

MR. SINCLAIR: I will have to refer that question to Dr. Schuller.

DR. SCHULLER: In one case rosin was reacted with sodium hydroxide making the sodium salt. Then we stripped off the turpentine. This prevented the levopimaric acid from isomerizing. Next the material was washed up with dilute acid. In this way we had a rosin with essentially the same levopimaric acid content as the original pine gum. In another case we followed a procedure worked out by John Lewis in Dr. Hedrick's group. Here we reacted pine gum with ammonia to make the salt. This was then washed thoroughly with a hydrocarbon solvent, preferably pentane. The solid is filtered and regenerated the acid. This removed most of the neutrals. The product contained most of the original levopimaric acid and was free of most of the neutrals.

QUESTION: What was the approximate loading of SE 52 on the column?

MR. SINCLAIR: We used Gas Chrome Q–loaded with 3 percent SE 52. The column does not work unless it is air aged overnight in a 325° C. static oven. What probably happens to the Gas Chrome Q is that its siloxy chains crosslink in air as the result of oxidation of methyl groups. With polydimethyl siloxane the methyl groups oxidize rapidly above 200°. The column was developed by Elmer Hinnenkamp of Battelle. If the column is not cured in air, it bleeds badly at 300-350° with nearly complete eventual loss of the column coating.

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Boudreaux, Gordon J. – Cotton Physical Properties Laboratory

Bourdette, Vernon R. – Information Officer

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